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Investigation of a Novel Method for Polonium-210 Determination in Groundwater

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INVESTIGATION OF A NOVEL METHOD FOR POLONIUM-210 DETERMINATION IN GROUNDWATER

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ABSTRACT

A novel method was investigated for the quantification of ^{210}Po in water as an alternative to the standard method of spontaneous plating onto Ag disks followed by quantification with an alpha spectrometer. The novel method concentrated a 0.5L sample by MnO_2 co-precipitation followed by dissolution of the precipitate into a solution. Polonium-210 was separated from the solution and quantified in a column containing a 50:50 by volume mixture of Pb resin (Eichrom Technologies, Inc.) mixed with granulated CaF_2:Eu scintillator. The column containing ^{210}Po is quantified on a liquid scintillation counter without the introduction of liquid cocktail. The minimum detectable concentration (MDC) is 53 mBq/L for the novel method compared to 2 mBq/L for the standard method. This MDC of the novel method meets the WHO limit of 100 mBq/L, but is significantly higher than the standard method. Polonium-210 concentrations were determined for five groundwaters from locations in upstate region of South Carolina and Nevada. The ^{210}Po concentration as determined for the novel method ranged from <MDC to 3703.0 mBq/L. Correlation between the concentrations found by the standard and novel methods was not good. In every case where the concentration was above the MDC, the concentration determined by the novel method trended higher, ranging from 37.2% to 90.3 %. In most cases, the higher concentration was attributed to uranium in the groundwater. Due to high variability in the background for the novel method columns, there is significant uncertainty in the concentrations determined by the novel method.

DEDICATION

This thesis is dedicated to my father. His encouragement and love of science inspired me to begin, and most importantly, finish this degree. I love you, Dad.

ACKNOWLEDGMENTS

I would like to thank the Department of Energy REAP program for partially funding my research, Dr. Timothy DeVol for all of your help and guidance, and my father for all of your help and encouragement. I would also like thank all of my lab and classmates, especially Todd Miller for all of your help with my resin columns and the ICP-MS.

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CHAPTER ONE

INTRODUCTION

Polonium-210, discovered by Marie Curie in 1898, is an alpha emitting progeny of ^{226}Ra, which is a progeny of ^{238}U. As ^{238}U is found naturally in the environment and is ubiquitous in the earth's crust, ^{210}Po can be found in trace amounts in nature, particularly in locations with uranium and radium ore deposits. Polonium-210 is created by neutron bombardment of ^{209}Bi in a nuclear reactor [Health Physics Society, 2007] with an annual production of 100 grams [RSC Chemistry World, 2006]. Polonium-210 emits a 5.3 MeV alpha particle, has a 138.4 day half-life, and decays to ^{206}Pb [Figgins, 1961]. Polonium-210 is very radiotoxic due to very high specific activity (166 TBq/g) [Health Physics Society, 2007] and large dose conversion factor for ingestion and inhalation. Even small amounts of ^{210}Po cause significant biological damage once inside the body. It is estimated that 22% of the total dose to humans in a year is due to ^{210}Po from the ingestion pathway [UNSCEAR, 2000]. The World Health Organization Guideline for ^{210}Po in drinking water is 2.7 pCi/L [WHO, 2006]. Although the EPA has not yet set a regulatory limit for water, ^{210}Po was added to the list of Contaminants Needing Research on Methods in 2001 [U.S. Environmental Protection Agency, 2001].

Polonium-210 is primarily used for static elimination in industrial settings. Polonium-210 is an effective static eliminator as it is a pure alpha emitter which can ionize surrounding air. While not as prevalent, ^{210}Po is also used in medical and academic research [Health Physics Society, 2007]. Although it has not been widely

used, ^{210}Po is also an excellent poison as microgram quantities of ^{210}Po can be fatal when ingested [Harrison et al., 2007].

The current methods for quantify polonium in water samples is fairly straight forward but are time-consuming. As ^{210}Po is found in trace amounts in natural waters, it must be concentrated from large water samples before it can be quantified. The goal of this work is to develop a method that would reduce the time necessary to process environmental water samples, with the hope that with small modifications that the procedure would also be applicable for bioassay samples. The inspiration for this thesis research came after the ^{210}Po poisoning of Alexander Litvinenko in November of 2006 as a significant back log of bioassay samples to be analyzed occurred due to the lengthy procedure and a few number of labs capable of conducting the analyses.

CHAPTER TWO

LITERATURE REVIEW

2.0 Review of ^{210}Po Determination Methods

Although there are a variety of published methods for ^{210}Po determination in groundwater, most outline a similar technique with small variations. Matthews et al., (2007) composed a detailed comparison of the available methods for ^{210}Po determination with the advantages and disadvantages of each procedure. Figure 1summarizes the general steps for ^{210}Po analysis with the solid line indicating the traditional and most often utilized method [Matthews et al., 2007].

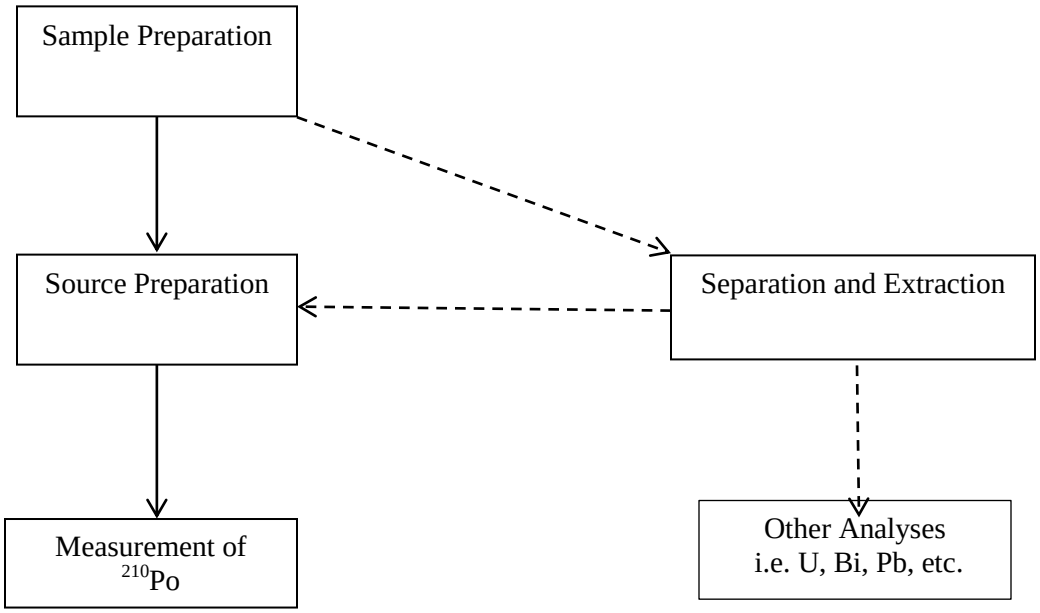


Figure 1: General Steps for ^{210}Po analysis [Matthews et al., 2007]

2.1 Sample Preparation

2.1.1 Collection and Tracer Selection

The first step of sample preparation is the water sample collection. The stable oxidation state of ^{210}Po in nature is +4, and exists as a hydrolyzed species that will easily absorb to solid surfaces [Katzlberger et al., 2001]. Because of the possibility of sorption, it is very important to acidify the water to a pH of 2 or below to prevent sorption to the sample container. Polonium-210 in groundwater can be supported or unsupported, based on the presence of ^{210}Pb, its grandparent in the ^{238}U decay chain. In the case of supported ^{210}Po (when ^{210}Pb is present), ingrowth of ^{210}Po in addition to ^{210}Po decay must be considered for the time between collection and sample analysis [Seiler, 2010]. For this reason, the time between collection and analysis must be closely monitored, and ^{210}Pb is often analyzed in conjunction with ^{210}Po.

When possible, it is then necessary to select a chemical tracer to account for loses. For methods utilizing alpha spectroscopy, ^{208}Po and ^{209}Po are commonly used tracers [U.S. Department of Energy, 1997; Ham et al., 1997]. Although historically ^{208}Po (5.115 MeV) has been the tracer of choice, ^{209}Po (4.883 MeV) has a longer half-life, and one can achieve better peak resolution due to the greater energy difference from the alpha particle emitted by ^{210}Po (5.304 MeV) [Matthews et al., 2007]. For methods utilizing other modes of quantification, such as liquid scintillation counting (LSC), it may not be feasible to utilize an isotopic tracer, as it is impossible to resolve the tracer and the ^{210}Po peaks [Véronneau et al. 2000]. For situations where ^{208}Po or ^{209}Po are not available or cannot be used, the method of standard additions can be used to determine ^{210}Po

concentration. The method of standard additions uses multiple known additions of an analyte of interest, in this case ^{210}Po, to a solution that contains an unknown analyte concentration [Harris, 2003]. The increase in activity measured in each solution is then compared to the activity added, and can then be used to linearly extrapolate the unknown concentration, where the y-intercept is the fitted count rate in the unknown sample and the slope term is the fitted yield and detection efficiency for the set. The method of standard additions is described in detail in the Materials and Methods section.

2.1.2 Concentration

The next step of sample preparation is generally a concentration step. For all methods using alpha spectroscopy, the aim of this step is to concentrate the water to a small volume (0.01-0.1M) HCl solution for spontaneous deposition on a metal disk [Matthews, 2007].

2.1.2.1 Evaporation

For many standard methods, concentration is performed by evaporating large water samples (~1L) acidified with HCl to a greatly reduced volume or near dryness [Matthews, 2007; Martin et al., 1998; Smith and Hamilton, 1984]. Special care must be taken during this step to prevent the sample from reaching total dryness as this will cause sorption of ^{210}Po to glass [Smith and Hamilton, 1984]. The U.S. Department of Energy (1997) outlines a procedure using 1 L of water evaporated to 20 mL, while Desideri et al. (2007) propose a method of determination with concentration achieved by evaporation of 1 L of water to 200 mL.

2.1.2.2 Co-precipitation

Co-precipitation is another common mode for concentration. There are variety of co-precipitants in the literature, however, $Fe(OH)_3$ and MnO_2 are most commonly used [Matthews et al., 2007]. $Fe(OH)_3$ co-precipitation can be performed using $FeCl_3$ and NH_4OH [Jia et al., 2001], NaOH, $NH_4OH + CaCO_3$, or $NH_4OH + Na_2CO_3$ [Matthews et al., 2007]. MnO_2 co-precipitation is performed with $KMnO_4$ and $MnCl_2$ [Kim et al., 2009; Carvalho, 1997; Martin and Hancock, 1992; Skwarzec et al., 2001]. Polonium-210 can also be precipitated using a Te carrier from a $SnCl_2$ solution [Rushing, 1966], bismuth phosphate (a method often used for transuranics [Holgye, 2007]), and by cobalt-ammonium pyrrolidine dithiocarbamate (Co-APDC) chelate [Wildgust et al., 1998].

2.2 Separation and Extraction

For the standard methods using evaporation, separation/extraction is typically not necessary; however, this step is an important step with co-precipitation, where spontaneous plating may be inhibited by interferences, and/or methods that quantify other radionuclides in addition to ^{210}Po [Matthews et al., 2009].

2.2.1 Solvent Extraction

Polonium separation and purification may be achieved through solvent extraction. Although Po has four expected oxidation states (-2, +2, +4, and +6), only the +4 is stable in solutions. In HCl solutions, Po is assumed to be $PoCl_6^{-2}$ [Martin and Hancock, 1992]. Based on this chemistry, there are a wide variety of extractants used in the literature that yield excellent results for separating Po from Pb and Bi, as well as other radionuclides. These include diethylammonium diethyldithiocarbamate (DDTC), diethyl

dithiocarbamate (DDC), Tri-isoctylamine (TIOA), and tricytle phosphine oxide (TOPO) in toluene. Martin and Hancock, (1992) and Kim et al., (2009) used 0.1% DDTC in chloroform to selectively extract Po in HCl solutions from other radionuclides following concentration by co-precipitation with MnO_2 from groundwater samples. Wai and Lo, (1982) used DDC to separate Po from Pb in spiked HNO_3 solutions, Chen et al., (2001) recovered more than 99% of ^{210}Po after separations from ^{210}Pb in spiked HCl solutions using TIOA in xylene, and Jia et al., (2004) demonstrated a method to separate Po from U using TOPO in toluene for separation of Po in spiked HCl and HNO_3 solutions.

Uranium extraction was investigated using *cis,syn,cis*-dicyclohexyl-18-crown-6 ether with organic solvents in HCl solutions [Yakshin et al., 2009]. The distribution ratio is at a maximum in 8M HCl using nitrobenzene and 1,2-dichloroethane solvents, and decreases with decreasing molarity. In 2M HCl, the log of the distribution ratio for uranium with the nitrobenzene and 1,2-dichloroethane solvents is < 0.

2.2.2 Extraction Chromatography

Another common separation technique uses extraction chromatographic resin. Extraction chromatography uses the principles of liquid-liquid extraction and column chromatography to separate radionuclides [Horwitz, 1998]. Extraction chromatography resins are small beads (50-150µm) with liquid extraction solvents impregnated into the resin. Figure 2 from Eichrom, Inc. is a depiction of the surface of a resin bead. The stationary phase contains an extraction solvent and usually a diluent (both specific to each resin type) to help solubilize the extractant, while the inert support provides the bulk for the resin bead, and is made of silica or an organic polymer. The mobile phase is

generally an acid solution and controls the chemistry to facilitate the separations [Horwitz, 1998].

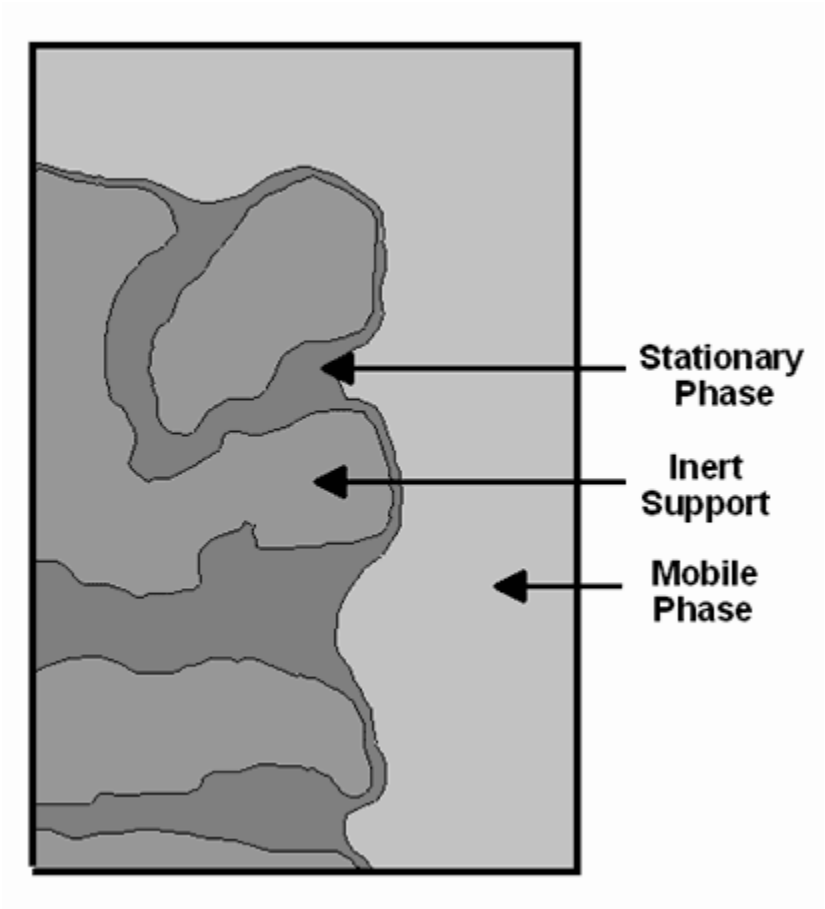


Figure 2: Surface of Porous Bead of Extraction Chromatography Resin [Eichrom Technologies, 2008]

It is necessary to determine the resin capacity factor, k', to characterize the behavior of a radionuclide on a resin in a particular mobile phase. The k' can be determined two ways. The first is calculated based on the number of free column

volumes at which the effluent concentration reaches or maximum, which corresponds to the elution of 50% of the analyte of interest [Roane and DeVol, 2005]. The second is found using a weighted distribution ratio, D_W. D_W is determined empirically by comparing the amount of activity initially in a solution to the amount sorbed to a known weight of resin after it has been in contact with the solution and equilibrium has been achieved. The results from this experiment can be inserted into Equation 1 to calculate D_W. In this Equation 1, A_0-A_s is the activity sorbed to a known weight of resin while A_s is the activity in a known volume of solution. Table 1, from Horwitz (1998), contains conversion factors for D_w to k' for a variety of resins which can be used for the k' calculation. These conversion factors were determined based on the typical ratio of the volume of the stationary phase to the volume of the mobile phase that is expected for columns packed with the particular resin of interest.

$$\boldsymbol{D_w = \frac{A_0 - A_s}{A_s}} \qquad (\mathbf{1})$$

Table 1: Conversion of D_w to k' [Horwtiz, 1998].

Resin	**To convert D_w to k' multiply by**
TEVA	1.9
UTEVA	1.7
TRU	1.8
Actinide	1.9
Sr	2.0

Vajda et al. (1997) proposed a method for polonium separation using the Sr extraction chromatography resin which uses elutions in HNO_3 and HCl for separation of

Po, Pb, and Bi. The Eichrom Sr resin uses the extractant, bis-4,4'(5')-tert-butyl-cyclohexano-18-crown-6 with 1-octanol as the diluent. As with many of the solvent extraction methods, this method was not performed on a ground water sample, but a spiked sample that did not require pre-concentration. Kim et al. (2009) combined the MnO_2 co-precipitation technique, with reconstitution of the precipitate in 1% H_2O_2 2M HCl, with the Po separation technique with Sr resin (as developed in Vajda et al. (1997)) to make the method applicable for water analysis. Figure 3 is a representation of the nitric acid dependency of Po (IV) and U (VI) on the Sr resin. Based on Figure 3, in low molarity HNO_3 (~1M) solutions, Po (IV) retention is at a maximum with a k' around 100 in 1M HNO_3 while U(VI) retention is negligible with a k' less than 1. Figure 4 is a chromatogram of the elution behaviors of Pb, Po, and Bi on the Sr resin under different chemical conditions. Polonium can be loaded onto the resin in 2M HCl, without retention of Bi, and can then be eluted using 6M HNO_3.

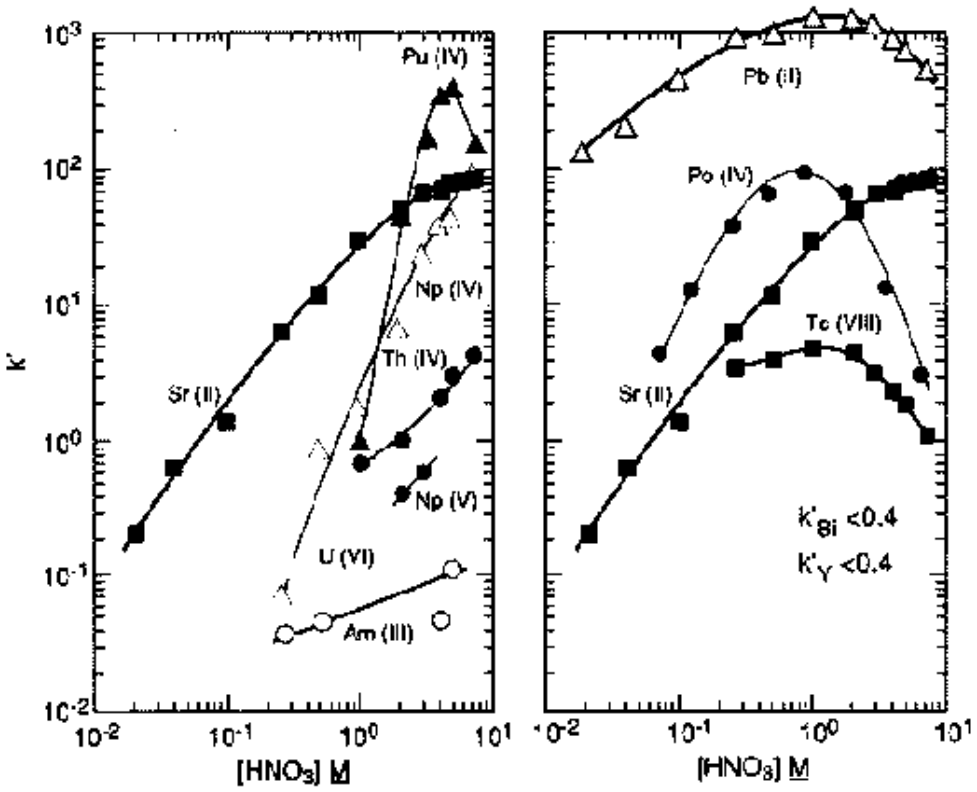


Figure 3: Acid Dependency of k' for various ions at 23-25˚C for Sr Resin [Horwitz, 1998]

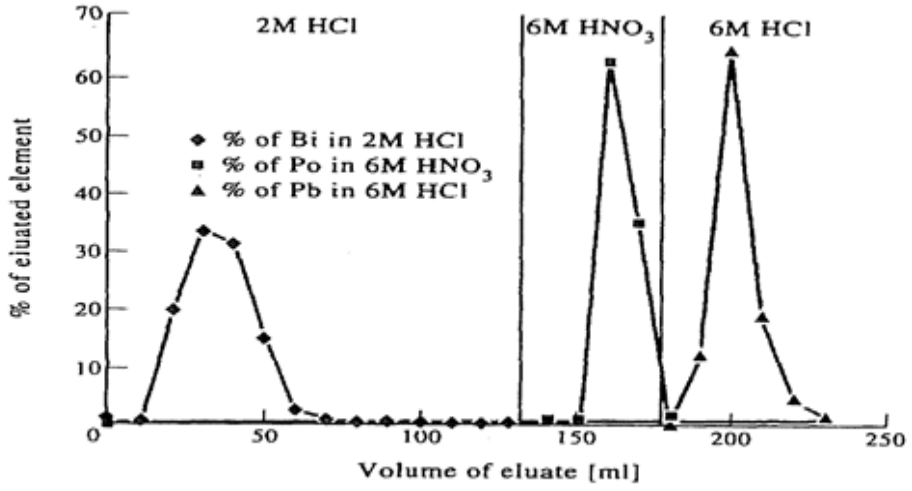


Figure 4: Elution chromatogram for Pb, Bi, and Po on Sr resin [Vajada et al., 1997]

In order to ease the stripping of ^{210}Pb from the extraction chromatography columns, Eichrom Technologies, Inc. developed a modification of the Sr resin called the Pb resin. This resin uses the same extractant in lower concentrations than in the Sr resin, and uses isodecanol as a diluent as opposed to 1-octanol [Eichrom Technologies, 2008]. The behavior of ^{210}Po on this resin is very similar to its behavior on the Sr resin, enabling them to be used somewhat interchangeably.

2.2.3 Ion Exchange Chromatography

Ion exchange chromatography has also been shown to separate and purify Po using both anion and cation exchange resins in HCl and HNO_3 solutions [Matthews et al., 2007; Danon and Zamith, 1957]. The anion exchange resins, Bio-Rad AG1-X4, which adsorbs polonium from acidic solutions [Reischmann et al., 1984] and the Dowex-1 and Dowex-2 resins can be used to separate Po, Pb, and Bi [Figgins, 1961]. Adsorption of Po has also been achieved using the cation exchange resin Amberlite IR-120, with ion exchange decreasing with increasing molarity for HCl and HNO_3 solutions [Danon and Zamith, 1957].

2.3 Source Preparation

2.3.1 Spontaneous Deposition

After a water sample has been concentrated, and when applicable separated and purified, a source for quantification can be prepared. The overwhelming choice for source preparation in the literature is spontaneous deposition onto a metal disk, from a heated, acidic solution. There is a wide variety of methods that utilize different metals, volumes, pHs, temperatures, and plating times. In spite of the numerous variations, excellent

yields are reported for most methods with typical ranges of 70-98% reported [U.S Department of Energy, 1997; Matthews et al., 2007; Smith and Hamilton, 1984; Jia et al., 2004]. Fe^{3+} interferes with polonium plating and must be reduced to Fe^{2+}, typically with ascorbic acid. Polonium has been shown to spontaneously deposit on copper, nickel, bismuth, and silver [Figgins, 1961]. However, silver is primarily used in the literature, as Pb and Bi may also plate on the other metals inhibiting Po deposition [Matthews et al. 2007].

The highest overall yields were reported for the methods utilizing the standard evaporation method. The Department of Energy deposition solution was made by adding 100 mL of DDI water and ascorbic acid to the 20 mL concentrated water solution, followed by plating on Ni disks at 55˚C for 2.5 hours with yields of 70% reported [U.S. Department of Energy, 1997]. For the Desideri et al. (2007) procedure, the plating solution was prepared by adding ascorbic acid and adjusting the solution to a pH between 1 and 2, followed by depositing on Ag disk at 85-90˚C with a mean yield of 70.9% reported. Of the literature surveyed for the standard method, the highest reported yield (95%) was by Smith and Hamilton (1984) who deposited on a Ag disk, from a pH 1.5-2 solution at 80°C for 2 hours.

Excellent yields have also been obtained by these methods utilizing separation and extraction. However, there is more variation in the yields reported for these methods. Vajda et al. (1997) plated ^{210}Po onto a Ag disk at pH 1 solution with ascorbic acid at 80˚C for 1.5 hours after separation with Sr resin. Overall yields between 50 and 70% were reported. Kim et al. (2009) using the combination of co-precipitation with MnO_2

and purification with Sr resin, plated on a Ag disk as well with a pH 1-2 solution, containing ascorbic acid, for 90 minutes at 90˚C with overall yields of 50-70%. Also following co-precipitation, Kim et al. (2009) and Martin and Hancock (1992) used DDTC in chloroform for Po separation. Using the same plating procedure utilized for the extraction chromatography method, Kim et al (2009) reported overall yields between 54-97%, averaging at 82%, while Martin and Hancock (1992) plated with Ag disks, at 70-80°C for 2 hours and reported yields of 95%. Jia et al. (2004) who used TOPO in toluene to separate Po from U in HCl and HNO_3 solutions, plated from a 1.5 pH solution on a Ag disk for 6-7 hours at 85-95°C with yields ranging from 64.7-97.9% depending on the acid (HCl or HNO_3) and dilution of acid (0.01M-10M) used.

2.3.2 Extractive Liquid Scintillation

Veronneau et al. (2000) demonstrated a method to selectively extract Po directly into an extractive liquid scintillation cocktail for quantification with an ORDELA, Inc. Photon-Electron Alpha Liquid Scintillation (PERALS) system. Veronneau et al. (2000) used URAEX cocktail, which contains triocytlamine (TNOA) to separate Po from the actinides in a 3M H_2SO_4-NaCl solution with yields up to 100% reported. Jokelainen et al. (2010) investigated the use of three extractive liquid scintillation cocktails, polonium extractive scintillator (POLEX), TNOA, and TOPO. Polonium-210 was effectively extracted using these solvents from spiked DDI water samples without the co-extraction of ^{238}U and ^{234}U. However, in actual groundwater containing ^{238}U and ^{234}U, both were co-extracted which interfered with ^{210}Po quantification.

2.3.3 Scintillating Extraction Chromatography

Clemson University in collaboration with Eichrom Technologies, Inc. developed scintillating version of some extraction chromatography resins which can not only be used for separation and purification but for counting samples as well. In addition to the organic polymer containing the extractant and the diluent, these resins also contains the fluors 2,5-diphenyloxazole and 1,4-bis(4-methyl-5-phenyloxazole-2-yl)-benzene [DeVol et al. 2001]. These fluors will allow the column to be counted directly on a liquid scintillation counter without elution and the addition of liquid scintillation cocktail. Although these resins have not been used for ^{210}Po separation and quantification, good results were obtained for other radionuclides. In addition to the homogeneous resins embedded with fluors, mixed beds containing extraction chromatography resin mixed with powdered scintillators, such as BC400 and yttrium silicate (YSO) for the detection of ^{241}Am, ^{237}Np, and natural uranium were studied as well [DeVol and Hughes, 2003]. DeVol et al. (1996) evaluated the scintillator CaF_2:Eu for use separating and quantifying ^{233}U, as U had been shown to adsorb to the scintillator. However, sorption decreased with decreasing pH, with very little adsorption at pH 2 [DeVol et al., 1996].

2.4 Measurement of ^{210}Po

2.4.1 Alpha Spectroscopy

Alpha spectroscopy is a technique for quantification of alpha particles using a silicon diode semiconductor detector [Knoll, 2010]. These detectors operate in a vacuum to enable them to detect alpha particles emitted from a source without degradation of the alpha particle energy. These particles are transformed into electrical pulses which are

amplified and shaped prior to conversion into a differentiated pulse height spectrum by a multichannel analyzer. The resultant spectrum is characteristic of the energy of the originally alpha particle. This technique is excellent for differentiation of alpha emitters due peak resolutions of as low 10 keV [Knoll, 2010] with typical resolutions of 25-30 keV [Matthews, et al., 2007]. The detection efficiency is relatively poor (3-20%), but because of the inherently low background (less than one count per hour in carefully controlled systems [Knoll, 2010]) the method has a high sensitivity for detecting alpha particles.

2.4.2 Scintillation Counting

2.4.2.1 Liquid Scintillation Counting

Liquid scintillation counting (LSC) is a technique for quantification of radioactivity in aqueous solution by conversion of alpha, beta, or gamma energy into photons. These photons are captured, converted into electrical pulses, and amplified by a photomultiplier tube. The relationship between the energy of the photon and the energy of the original particle is linear, which enables the user to extrapolate the energy of the original photon [Kessler, 1989]. Although the detection efficiency for alpha particles is around 100 %, the peak resolution is poor (~1 MeV), due to low photon yields which inhibits its use for differentiation of different alpha emitters [Kessler, 1989]. Veronneau et al. (2000) used an ORDELA, Inc. PERALS system for LSC, which is specifically designed for alpha emitters and extractive scintillating cocktails. It has better energy resolution (~300 keV) than normal liquid scintillation counters, a 99.7% detection

efficiency for alphas, and 99.95% rejection capability of unwanted pulses from electrons and photons with a background count rate of 0.001dpm [ORDELA Inc., 1997].

2.4.2.2. Solid Scintillation Counting

Solid scintillation counting uses the same principles and similar equipment as LSC, but utilizes solid scintillators instead of liquid scintillation cocktail. There are a variety of solid scintillators available. These include the crushed scintillators YSO [DeVol and Hughes, 2003], CaF_2:Eu [DeVol et al., 1996], BC-400 scintillating plastic beads [DeVol and Hughes, 2003], and resins impregnated with scintillating fluors [DeVol et al., 2001]. The detection efficiency for alpha particles in solid scintillation counting is lower than that of LSC and is dependent on the scintillator selected and the geometry of the column or tubing containing the scintillator. DeVol et al. (1996) reported detection efficiencies of 68% for ^{233}U for CaF_2:Eu in a 1.5mm inner diameter polytetrafluoroethylene tubing.

2.4.3 Minimum Detectable Concentration

The minimum detectable concentration (MDC) is determined using Equation 2 and 3. The lower limit of detection (LLD) is determined by Equation 3, t is the count time, Y is the chemical yield, $\boldsymbol{\varepsilon}$ is the detection efficiency, f is the decay fraction (equal to 1 for ^{210}Po), and V is sample volume [Knoll, 2010; Cember and Johnson, 2009]. For methods utilizing alpha spectroscopy for quantification, where the background count rate and ε should be similar in different systems, the variants affecting the MDC are the count time, sample volume, and sample yield. As the majority of the methods surveyed in this section reported similar yields (between 70-95%) and used similar sample volumes (1L),

there would not be a significant variation in the MDC (~1mBq/L for a 1000 minute count time) for the methods, assuming the same count time. Veronneau et al. (2000) did not use alpha spectroscopy but a liquid scintillation counter for Po quantification. Although liquid scintillation counters typically have higher background count rates, Veronneau et al. (2000) used an ORDELA, Inc. PERALS system which is specifically designed to detect alpha particles and the reject unwanted pulses from electrons and photons. Because of the use of this system and chemical yields around 100%, Veronneau et al. (2000) reported an MDC of 1mBq/L for a 1000 minute count time.

$$MDC = \frac{LLD}{t\varepsilon fYV} \quad \textbf{(2)}$$

$$\mathrm{LLD} = 2.71 + 4.65\sigma_{\mathrm{Background}} \quad \textbf{(3)}$$

2.5 Summary

The methods discussed in this chapter are summarized in Figure 5. The first three steps in a ^{210}Po detection method are common to all ^{210}Po methods. The steps on the left side of the figure summarize the standard and most widely utilized method, while the steps on the right summarize other methods available methods.

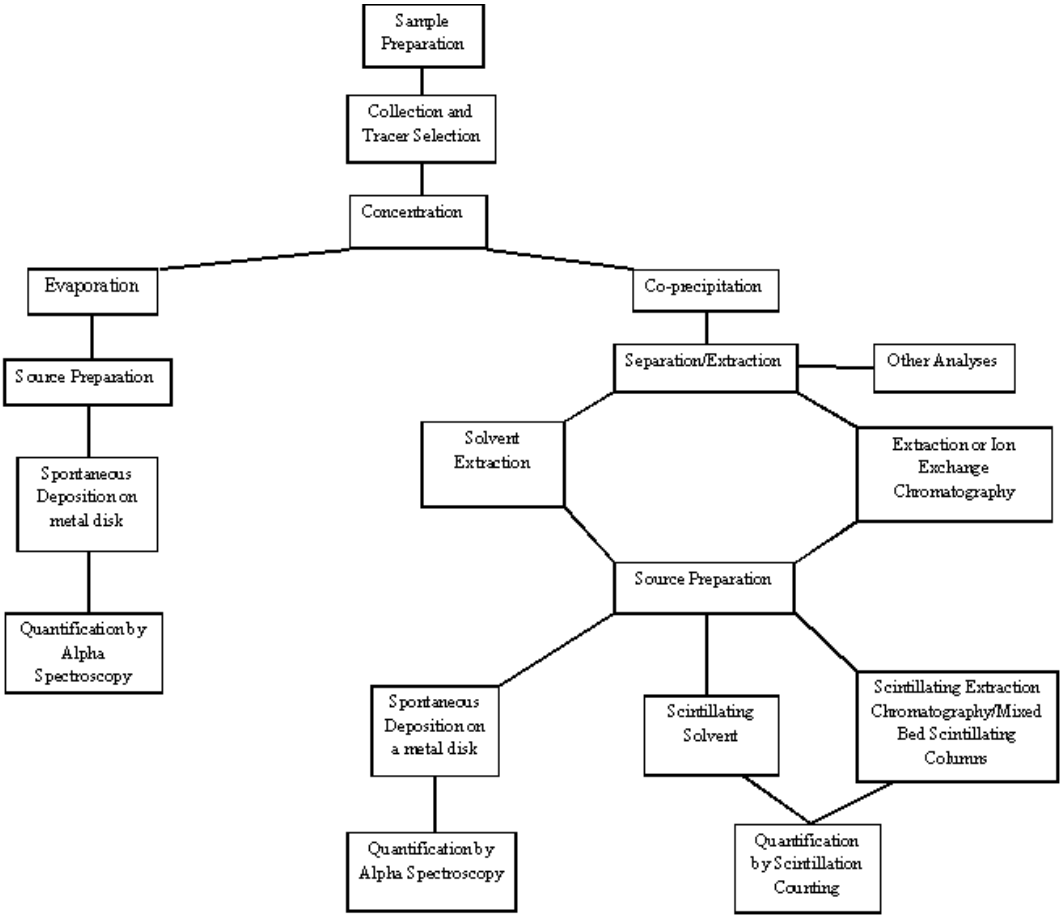


Figure 5: Summary of ^{210}Po detection Methods

CHAPTER THREE

RESEARCH OBJECTIVES

The primary objective of this work is to investigate a novel method ^{210}Po determination in groundwater while maintaining accuracy and reproducibility. The desired quantification limit for this technique is 100 mBq/L (2.7 pCi/L), the World Health Organization limit for ^{210}Po in groundwater [WHO, 2006].

Task 1

- Investigate a ^{210}Po concentration method
    - Investigate the use of co-precipitation with MnO_2.
    - Characterize the behavior of Po on the Pb and Sr extraction chromatography resin with HCl as the reagent.
- Develop a ^{210}Po quantification method
    - Investigate scintillating extraction chromatography resin or mixed bed scintillator-extraction chromatography resin mixtures.

Task 2

- Compare novel method with standard method of ^{210}Po determination
    - Comparison of five natural water samples

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Polonium Standard Preparation

A ^{210}Po standard was prepared in-house using a modification of Vajda et al. (1997) purification procedure with an Eichrom Sr extraction chromatography resin. An "old" ^{226}Ra (11.9nCi on 3/91) source was reconstituted in 3 mL of 2M HCl (BDH Aristar ACS, NF, FCC Grade). A 2 mL Eichrom pre-packed Sr resin column (100-150 µm) was washed with 75 mL of DDI water, followed by 75 mL of 1M HNO_3, then followed by 75 mL of 2M HCl with a flow rate of about 0.5 mL per minute. The radium source in 2M HCl was passed through the column. ^{226}Ra and ^{210}Bi were eluted with 74 mL of 2 HCl and saved in one vial, and ^{210}Po was eluted with 37 mL of 6M HNO_3 (Note: All HNO_3 used in these experiments was Fisher Chem Alert Trace Metal Grade) and saved in another vial. The ^{210}Pb was not be eluted from the column, and the column was saved for future milking of ^{210}Po as needed and ingrowth allowed. The purified ^{210}Po in 6M HNO_3 was slowly evaporated to near dryness and reconstituted in 10 mL of 2M HCl. The evaporation/reconstitution of ^{210}Po in 2M HCl is repeated two additional times. Finally, the ^{210}Po was reconstituted in 30 mL of 2M HCl. A small aliquot (0.1000g) of the prepared ^{210}Po was mixed with 20 mL of PerkinElmer Optiphase HiSafe 3 liquid scintillation cocktail (Note: the same liquid scintillation cocktail was used in all experiments). This sample was counted on the Perkin Elmer Wallac Quantulus 1220 (#2200339) to determine the standard ^{210}Po concentration. (note: All LSC was performed on this instrument.) The ^{210}Po concentration was determined to be 162.6 ± 0.3Bq/g. To

ensure the ^{210}Po is successfully separated from the other progeny, 1 mL of the standard was evaporated on a planchet and counted on an AMETEK, Inc. ORTEC Octet Plus Alpha Spectroscopy System (note: All alpha spectroscopy was performed using this system).

4.2 Water Sample Collection and Site Selection

As part of a laboratory course at Clemson University entitled Environmental Radiation Protection (EE&S 813), high levels of U were discovered in natural well waters in upstate South Carolina, Table 2. As ^{210}Po is a progeny of ^{238}U, these wells and others in the area were selected for ^{210}Po analysis. Seiler et al. (2007) found abnormally high levels of ^{210}Po in natural wells in Lahontan Valley, Nevada with concentrations as high as 67.7 pCi/L detected. Due to the high levels of natural unsupported ^{210}Po one of the wells from this site was also selected for analysis.

Table 2: ^{238}U concentration determined by ICP-MS [EE&S 813, 2008]

Sampling Location	**U-238 (ppb)**
Table Rock State Park	1.635 ± 0.806
Devil's Fork State Park	18.850 ± 1.439
Round House Point	338.249 ± 15.569

The stable oxidation state of ^{210}Po in nature is +4, and exists as a hydrolyzed species that will easily absorb to solid surfaces [Katzlberger et al., 2001]. Because of the possibility of sorption, it is very important to acidify the water to a pH of 2 or below to prevent sorption to the sample container. Five gallons from each sample location were

collected and immediate acidified to pH 2 with 12M HCl. To insure the samples collected were a good representation of the groundwater, the water was allowed to flow until the temperature had stabilized before samples were collected.

4.3 Standard Additions

The method of standard additions was used to calculate the concentration of ^{210}Po in groundwater. This method uses multiple known additions of an analyte of interest, in this case ^{210}Po, to a solution that contains an unknown analyte concentration [Harris, 2003]. This method can be performed with one spiked and one unspiked water sample. More precision can be achieved by using additional analyses so one unspiked and three spiked, at varying levels, water samples were selected for the standard method. The data is graphed as the gross count rate versus the activity added. The increase in activity measured in each solution is then compared to the activity added and can then be used to linearly extrapolate the unknown concentration. The y-intercept is the count rate of the unknown sample and the slope is the product of the yield and detection efficiency for the sample set. Figure 2 is a standard additions graphical example. Error analysis can be performed based on a method by Rogers, (1975). This method uses a minimization of χ^2, the difference between the experimental activity and the activity determined based on the fit equation, to determine the optimum y intercept and slope for the data set. After the χ^2 minimum (χ^2_{min}) has been determined, errors in the y-intercept and slope term are obtained by individually altering the y-intercept and slope term until $\chi^2 = \chi^2_{min} + 1$.

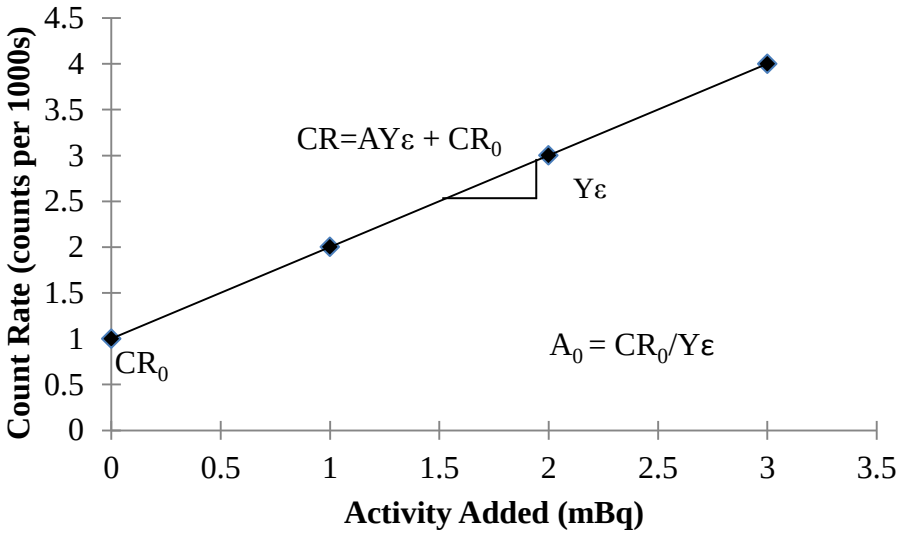


Figure 6: Graphical example of standard additions

4.4 Standard Method for Polonium Determination

The procedure selected for comparison with the novel method that was developed is a modification of the Department of Energy method; hence forth referred to as the standard method. The DOE method employs a ^{209}Po tracer to determine sample yields; however, a ^{209}Po tracer was not available for these experiments. Therefore, ^{210}Po concentrations were determined using the method of standard additions. Four 500 mL water samples were obtained from each sampling location. The samples from each location were spiked with either 15 mBq, 25 mBq, or 50 mBq with the exception of the Nevada samples which were spiked with either 250 mBq, 750 mBq, or 1000 mBq. These concentrations were determined based on a scoping experiment to estimate the sample activity for each location. This scoping experiment followed the same procedure outlined in this section with one spiked and one unspiked sample from each sampling location.

The spiked sample from each location was spiked with 0.5 Bq with the exception of the Nevada sampling location which was spiked with 3 Bq.

After all applicable samples were spiked with ^{210}Po, the sample concentration step began. Twenty-five mL of 12M HCl was added to each 500 mL sample (previously preserved at pH 2) which was then evaporated to 20 mL. One hundred mL of DDI water was added, as well as 100 mg of ascorbic acid (Mallinckrodt U.S.P Lot 4407 KLND) to reduce ferric iron. For plating, the solution was adjusted to pH 1 (note: all pH adjustments were performed using HCl and NH_4OH (Alfa Aesar Environmental Grade and the Thermo Scientific ORION 8175BNWP ROSS Sure Flow Semi Micro pH probe) and placed in a water bath at 80˚ C. The DOE method does not call for a pH adjustment as the pH of the solution should already be between 0 and 1; however, all samples were adjusted to 1 to assure sample uniformity. The DOE method also plates in a 55° C water bath, however, the higher temperature water bath was selected for this experiment as the literature suggests higher sample yield in higher temperatures [Matthews et al., 2007]. A clean, unoxidized ¾in. diameter silver disk (A.F. Murphy Die and Machine Co., Inc.) was rinsed with 80% ethanol, dried, and suspended in the sample for two hours while the solution was agitated with a stir bar. The DOE method plates using Ni disks, however, Ag disks were selected for plating in this experiment as the literature suggests higher yields for samples plated on Ag [Matthews et al., 2007]. The silver disk was then removed, rinsed with DDI water, allowed to dry, and counted using alpha spectroscopy.

4.5 k' (Capacity Factor) Determination

The capacity factor, k' was determined for the Pb extraction chromatography resin (Eichrom Technologies, Inc.), CaF_2:Eu independently, and the 50:50 mixture of CaF_2:Eu-Pb resin to determine the polonium retention to each material or mixture in a solution of 2M HCl + 0.015M Ca^{2+}, prepared using $Ca(NO_3)_2$. The amount of Ca^{2+} added to the solution was determined based on a CaF_2:Eu solubility experiment discussed below in section 4.6.1. For the Pb resin and the 50:50 CaF_2:Eu-Pb resin mixture, 0.1-0.3 g of Pb extraction chromatography resin (100-150 µm) or 0.5g of the 50:50 by volume mixture of Pb extraction chromatography resin mixed with CaF_2:Eu (crushed and sieved to <47 µm), referred to as the CaF_2:Eu-Pb resin mixture, was dry packed in a 10 mL BIORAD Poly-prep chromatography column. The columns were conditioned with 10 mL of DDI water and 10 mL of 2M HCl with 0.015M Ca^{2+}. Columns were spiked with a known amount of ^{210}Po activity then washed with 2M HCl with 0.015M Ca^{2+} in 1 mL increments. The effluents from the spike load and from each 1 mL 2M HCl with 0.015 Ca^{2+} wash were collected in plastic liquid scintillation vials, mixed with 19 mL of liquid scintillation cocktail, and counted on the Quantulus. For the independent CaF_2:Eu k' experiment, the conditions above were followed using 0.5 g of CaF_2:Eu without any resin addition. The k' for all experiments was determined based on the volume of 2M HCl with 0.015M Ca^{2+} wash through the column at which half of the spiked activity had been removed.

4.6 CaF_2:Eu Investigation

4.6.1 Solubility of CaF_2:Eu in 2M HCl

The solubility of CaF_2:Eu in 2M HCl was investigated due to visible dissolution during CaF_2:Eu-Pb resin mixture column conditioning. Three replicate samples were prepared using 0.5g of CaF_2:Eu with 20 mL of 2M HCl. The samples were shaken for 30 minutes and centrifuged sufficient to remove <47µm particles from the aqueous phase. One and one half mL of each sample was then collected. This was repeated after 60 and 90 minutes of shaking time. 0.1 mL of each 1.5 mL collected was diluted with 9.9 mL of 2% HNO_3 (Ultra-Pure Fischer Optima) for analysis on the ICP-MS (Thermo Scientific X Series 2). In preliminary studies, there was some dissolution in the 2M HCl so a solubility test was performed on the CaF_2:Eu in 2M HCl. Based on 90 minutes of contact time with the CaF_2:Eu and the acid, the average dissolved Ca^{2+} concentration was 0.587g/L or 0.015M. To limit dissolution, all 2M HCl used for the column experiments was doped with 0.015M Ca^{2+} in the form of $Ca(NO_3)_2$ to saturate the acid with Ca^{2+} before contact with the CaF_2:Eu.

4.6.2 CaF_2:Eu-Pb Resin Detection Efficiency Determination

Detection efficiencies were investigated for 50:50, 60:40, 70:30, and 80:20 by volume mixtures of CaF_2:Eu-Pb resin. The same column conditioning and ^{210}Po loading procedure as above for the k' determination procedure was used. However, 1g of the CaF_2:Eu-Pb mixture was used instead of 0.5g. The column was washed with 2 mL of 2M HCl with 0.015M Ca^{2+}. The top of the column was removed, and the bottom of the column, containing the CaF_2:Eu-Pb resin mixture, was placed in a plastic liquid

scintillation vial and counted on the Quantulus without the introduction of liquid scintillation cocktail. The detection efficiency was determined based on the count rate from column less the background count rate compared to the known activity loaded onto the column.

4.7 Novel Method for ^{210}Po Determination

Polonium-210 was concentrated using $KMnO_4$ and $MnCl_2$ co- precipitation following the procedure of Kim et al. (2009). Using 500 mL of groundwater previously preserved at pH 2, 10 mL of 12M HCl was added. At this time, the same spike activities were added to each sample. All samples were agitated with a stir bar for 1 hr to ensure the spiked ^{210}Po was uniform throughout. Three mL of 0.2M $KMnO_4$ were added, the pH was adjusted to 9 using 11.1M NH_4OH, and 5 mL of 0.2M $MnCl_2$ were added to initiate the precipitation. The sample was stirred for 1 hour to ensure all of the precipitate had formed. The samples then sat overnight to allow the precipitate to settle. After settling, as much of the liquid as possible without losing the precipitate was suctioned out of the samples, and the remaining liquid and precipitate was transferred into 50 mL polypropylene centrifuge tubes. The samples were then centrifuged sufficient to remove particles down to 59 nm and the remaining supernatant was suctioned out of the tube. To make this method more rapid, immediately after the co-precipitation is completed the samples can be separated into 3 separate 250 mL centrifuge tubes and centrifuged. As much of the supernatant as possible without disturbing the precipitate was suctioned out of the centrifuge tubes while the precipitate and remaining supernatant from each 250 mL

tube can be transferred into a 50 mL polypropylene centrifuge tube. The samples can then be centrifuged and the remaining supernatant can be suctioned out of the tube.

Following centrifugation, the sample was prepared for loading onto the resin scintillator columns. The precipitate was dissolved in 10 mL of 1% H_2O_2 in 2M HCl + 0.015M Ca^{2+} solution followed by heating on a hotplate at 90˚ C for 30 minutes to degrade the H_2O_2. The concentrated solution was then passed through 1.6g of the CaF_2:Eu-Pb resin mixture dry-packed in a 10 mL BIORAD Poly-prep chromatography columns. The CaF_2:Eu-Pb resin mixture was washed with 10 mL of DDI water followed by 10 mL of the 2M HCl + 0.015M Ca^{2+} solution. The concentrated polonium from the co-precipitation was then passed through the column, maintaining a flow rate no faster than 0.5 mL per minute. After all of the concentrated polonium solution passed through the column, the column was washed with 6mL of the 2M HCl + 0.015M Ca^{2+} solution and then counted on the Quantulus for 12 hours without the introduction of liquid scintillation cocktail. Concentrations were determined using the method of standard additions, and were decay corrected to the time of collection. Four DDI water samples spiked with a known amount of ^{210}Po were also processed following this method to determine the yield and detection efficiency for this novel method.

The novel method was also performed on synthetic groundwaters. The synthetic groundwater was prepared using DDI water and the following a formula from Smith, et al. (1996): 16 ppm Ca^{2+}, 4.6 ppm Na^{+}, 23.5 ppm K^{+}, 48.8 ppm HCO^{3-} , 21.3 ppm Cl, and 9.6 ppm SO_4^{2-}. Four 500 mL solutions of synthetic groundwater were spiked with 18.4 mBq, 31 mBq, 42 mBq, and 55 mBq and processed using the novel method procedure

above. The yield and detection efficiency were determined based on the count rate from column compared to the known activity spiked into the DDI water. Three columns were also prepared using unspiked synthetic groundwater, and were counted for 12 hours on the Quantulus to establish the background count rate.

4.7.1 Column Elutions

Polonium-210 was eluted from one of the columns for each water sampling location due to the suspicion of radiological inferences. Each column was eluted with 6 mL of 6M HNO_3, and this effluent was collected in four separate planchets and evaporated using a heat lamp. After evaporation was complete, the samples were counted using alpha spectroscopy to determine if other alpha emitters were present in the columns and, if so, to quantify the activity of these alpha emitters.

4.7.3 Groundwater Gross Alpha Measurements

Gross alpha measurements were performed for each water sampling location after other alpha emitters were detected in the novel method column elutions. Five mL of each water sample was mixed with 15 mL of liquid scintillation cocktail for counting on the Quantulus for 48 hours.

4.8 Uranium Analysis

4.8.1 Uranium in Groundwater

Uranium analysis was performed on the groundwater from each sampling location. The water samples were already acidified with HCl, so 1.5 mL of each water sample was processed in the ICP-MS. The calibration standards on the ICP-MS were in 2% HNO_3, so another experiment was performed with 1.5 mL from each sampling

location adjusted to 2% HNO_3. This change had no effect on the U concentration determined by the ICP-MS.

4.8.2 Uranium Batch Uptake Experiment

Uranium batch uptake experiments were performed after U was detected in the novel method column elutions. Experiments were performed on Pb resin and CaF_2:Eu individually, as well as the CaF_2:Eu-Pb resin mixture in 2M HCl + 0.015M Ca^{2+}, 1M HCl + 0.0075M Ca^{2+}, 0.1M HCl + 0.00075M Ca^{2+}, and 0.000075M Ca^{2+}. Three samples one containing a half gram of the CaF_2:Eu-Pb resin mixture, one containing 0.4g of CaF_2:Eu only, and one containing 0.1g of Pb resin only were contacted with 10 mL of each acidic concentration spiked with 10 ppm ^{238}U for 45 minutes. The samples were transferred into Pall Microsep 30 K Micro Omega centrifuge tubes and centrifuged at 2000 rpm on a Beckman CS-6 centrifuge until all of the liquid had been filtered. Two mL of the centrifuged liquid for each sample was mixed with 2 mL of 4% HNO_3 solution to be analyzed on the ICP-MS.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Standard Method

5.1.1 Exploration of the Standard Method

Exploratory experiments for the standard method were performed to insure the results used for comparison to the novel method were as accurate as possible. The standard method for ^{210}Po quantification is concentration by evaporation, spontaneous deposition onto a metal disk from a heated, acidic solution, and quantification using alpha spectroscopy. The best results were achieved by using a silver disk, pH 1-2 solution heated to 80-90°C, with disk contact for at least 2 hours, according to the results obtained by these experiments and the data found in the literature. The standard method for comparison was selected from the exploratory data found in Appendix A. Table 3 is the yield determination data from the standard method, for spontaneous deposition using a small volume of DDI water spiked with ^{210}Po. The error in these values was determined based on counting statistics (raw data in Table A-1). The deposition solutions were prepared using a small water volume so a concentration step was not necessary. These values are consistent with the data found in the literature (70-95% [U.S Department of Energy, 1997; Matthews et al., 2007; Smith and Hamilton, 1984]).

Table 3: Yield determination for spontaneous plating portions of the standard method for experimental conditions at pH 1, 80°C, and 2 hour contact time.

Sample	Total Yield (%)
1	90.3 ± .92
2	89.4 ± .035
3	85.1 ± .037
4	72.5 ± .74
Mean	84.3
Standard Deviation	8.20

5.1.2 Standard method for groundwater

For groundwater samples where the ^{210}Po concentration is unknown, the method of standard additions was used to account for the variability in the chemical yield. The overwhelming choice in the literature is to use a ^{208}Po or ^{209}Po tracer to account for losses, but for these experiments a tracer was not available for use. Two different bottled groundwaters (labeled A and B), and one collected groundwater (labeled C) were analyzed for ^{210}Po. Three different bottles of groundwater "A" were obtained and analyzed. These bottles are from the same location and are therefore assumed to have the same ^{210}Po concentration. The analyses on these samples followed the standard method procedure for samples analyzed in duplicate. The yield and concentrations were determined by standard additions for duplicate samples, and this data is found in Table 4. The error on these results was determined based on counting statistics. Using the average yield from these experiments (47.2%), a typical detection efficiency of 16.3% for an alpha spectroscopy chamber using slot 2, and a 24 hour count time, the MDC (based on Equation 2) for this method was found to be 2.0 mBq/L (raw data in Table A-2).

Table 4: Standard method groundwater yield determination counted by alpha spectroscopy.

Groundwater Samples	Sample Activity (mBq)	Total Yield (%)
A Bottle 1	32 ± 4.4	37.5 ± 3.9
A Bottle 2	21.7 ± 3.1	52.7 ± 18.8
A Bottle 2	20 ± 4.5	42.2 ± 3.5
A Bottle 3	12 ± 1.2	67.7 ± 2.1
B	56 ± 3.7	39 ± 4.3
B	28.7 ± 6.2	44.6 ± 12.2
C	25.9 ± 1.0	47 ± 3.1
	Mean	47.2
	Standard Deviation	10.4

Polonium exists as a hydrolyzed species in groundwater, so upon sample collection, it is important to adjust the pH to 2 or below to minimize sorption to the holding container. Groundwater C was acidified within one week of collection, but the time between collection and acidification for the bottled groundwaters is not known. These samples were acidified as soon as they were obtained. Concentrations determined for these bottled groundwaters may not accurately reflect the true concentrations found in the water.

The yields from these experiments can be compared to the deposition results in DDI water in Table 3 and to each other. Compared to the DDI water samples, the average yield has been reduced by almost half, and the standard deviation of the data has increased. This could be attributed to losses during concentration, as the DDI plating solutions had not been concentrated from large samples. The increased variability in the yield could also be due to differences in the groundwater versus the DDI water. It is

noted that similar variability in the water samples from the same location have been reported. The mean yield from groundwater A is 50.0% with a standard deviation of 13.4%. This increased variability makes the use of an isotopic tracer more appealing. However, using the method of standard additions with additional analyses for the standard additions improves the precision of the measurements.

5.2 Novel Method Development

The novel method selected for development uses a mixture of extraction chromatography resin mixed and granulated scintillator. By utilizing these mixed bed columns, separation of ^{210}Po can be coupled with quantification on a liquid scintillation counter, which should reduce sample processing time. The initial idea for the novel method utilized a homogenous resin, containing the normal resin beads impregnated with a fluor. However, due to resin failure from an unknown cause, developing a heterogeneous mixed-bed resin method was selected. Spontaneous deposition onto ZnS:Ag disks and ^{210}Po loaded extraction chromatography resin sandwiched between two ZnS:Ag disks methods were also investigated. The data from these methods and the homogenous scintillating Pb resin method can be found in Appendix C.

5.2.1 Granulated Scintillator Selection

CaF_2:Eu was selected as the granulated scintillator for the mixed bed columns as it has been used in heterogeneous resin-scintillator mixtures. In preliminary studies, there was some dissolution in the 2M HCl so a solubility test was performed on the CaF_2:Eu in 2M HCl. Based on 90 minutes of contact time with the CaF_2:Eu and the acid, the average dissolved Ca^{2+} concentration was 0.587g/L or 0.015M. To limit dissolution, all 2M HCl

used for the column experiments was doped with 0.015M Ca^{2+} in the form of $Ca(NO_3)_2$ to saturate the acid with Ca^{2+} before contact with the CaF_2:Eu. ZnS:Ag and YSO scintillators were also investigated for use in the mixed bed columns, but could not stand up to the harsh acidic conditions. An efficiency optimization experiment (raw data in Table A-5 and A-6P) was used to select the ratio of CaF_2:Eu to Pb resin for the mixed bed columns. The efficiencies determined by this experiment are found in Table 5 with error determined based on counting statistics. A 50:50 by volume mixture of the resin and CaF_2:Eu was selected to maximize the amount of Pb resin while still achieving an acceptable efficiency.

Table 5: Detection and loading efficiencies for CaF_2:Eu-Pb resin mixture ratios.

Column Ratio (CaF_2:Eu:Pb Resin)	Loading Efficiency (%)	Detection Efficiency (%)
50:50*	100 ± 0.2	22.4 ± 3.7
60:40	99.6 ± 0.1	31.8 ± 0.1
70:30	99.7 ± 0.1	32.1 ± 0.1
80:20	99.6 ± 0.1	52.8 ± 0.1

*Calculated based on the average of 5 samples found below in Table 7

5.2.2 k' Determination

Eichrom Technologies, Inc. has published data for the k' of Po on the Sr resin as a function of HNO_3 concentration [Horwitz, 1998]. To date, Eichrom Technologies, Inc has published data for the k' of Po on the Pb resin in HNO_3 or the k' of Po as a function of HCl concentration for the Sr or Pb resin. As the heterogeneous resin-scintillator mixture will be counted in a liquid scintillation counter, the column containing the mixture must be small enough to fit in a liquid scintillation vial and detection efficiency

may be reduced by a thick column. This reduces the amount of resin that can be used, so a k' for the Pb resin in 2M HCl was needed to determine if the small amount of resin would be sufficient to isolate the Po. The data from the k' determination method for Pb resin is shown in Figure 7. The k' was calculated based on the number of pore volumes of 2M HCl at which half of the initial column activity added was removed from the column, as determined from the aliquots collected and counted on the Quantulus. From two separate k' experiments (raw data in Table A-5a and A-5b), the k' for the Pb resin column was 143 and 132. This test was also performed using the resin and the 2M HCl +0.015M Ca^{2+} (raw data in Table A-5c), and this data is included in Figure 7. With the addition of Ca^{2+} to the 2M HCl the k' was found to be 165. Assuming a variability of ± 11, as seen in the experiments in 2M HCl without the addition of Ca^{2+}, there is a small increase in the k' observed.

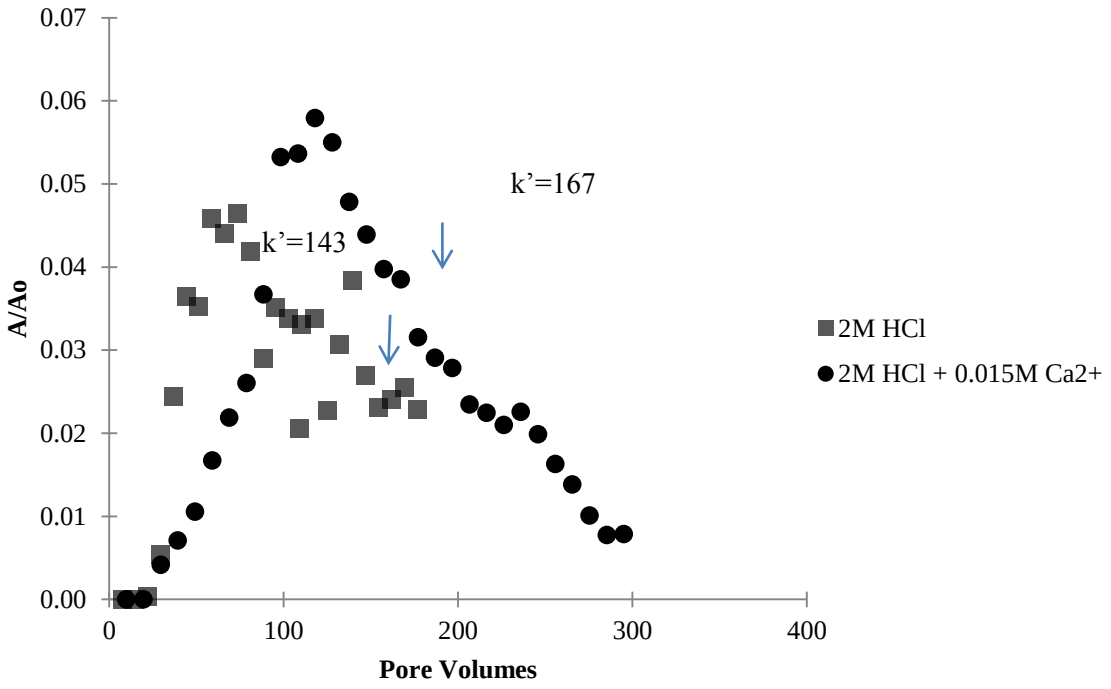


Figure 7: Activity/initial activity vs pore volume of Pb extraction chromatography resin column in 2M HCl and 2M HCl + 0.015M Ca^{2+} for k' determination.

Additional k' tests were performed to determine the Po retention on the CaF_2:Eu-Pb resin mixture column (raw data in Table A-5c) and on CaF_2:Eu individually in 2M HCl + 0.015M Ca^{2+} (adjusted with $Ca(NO_3)_2$) (raw data in Table A-5d). The k' for the CaF_2:Eu-Pb resin mixture column was found to be 137 pore volumes (Figure 8). The amount of resin in the column per pore volume is lower due to the 50:50 by volume mixture, and the k' was reduced by ~18%. This corresponds well to the data for the k' of the Pb resin alone in 2M HCl + 0.015M Ca^{2+}, which was shown to increase with the addition of $Ca(NO_3)_2$. The k' for Po on CaF_2:Eu alone in 2M HCl + 0.015M Ca^{2+} was only found to be 10, indicating that Po was not retained on CaF_2:Eu alone (Figure 9). Based on a convenient sized column, the maximum amount of the CaF_2:Eu-Pb resin

mixture that can be used is 1.6g which corresponds to 1 pore volume per 0.75 mL of solution. With a k' around 137 pore volumes and 5% loss around 29 pore volumes, this amount of resin and CaF_2:Eu is sufficient for isolation and quantification of ^{210}Po from a 15 mL solution, the volume of the concentrated ^{210}Po solution following co-precipitation. Additional supporting data for k' determinations can be found in Appendix B.

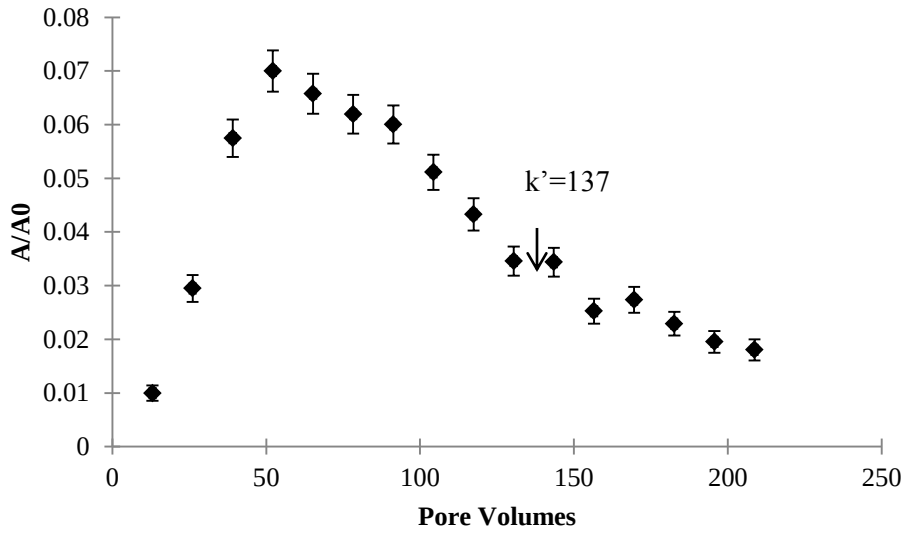


Figure 8: Activity/initial activity vs pore volume of CaF_2:Eu-Pb resin column in 2M HCl + 0.015 M Ca^{2+} for k' determination.

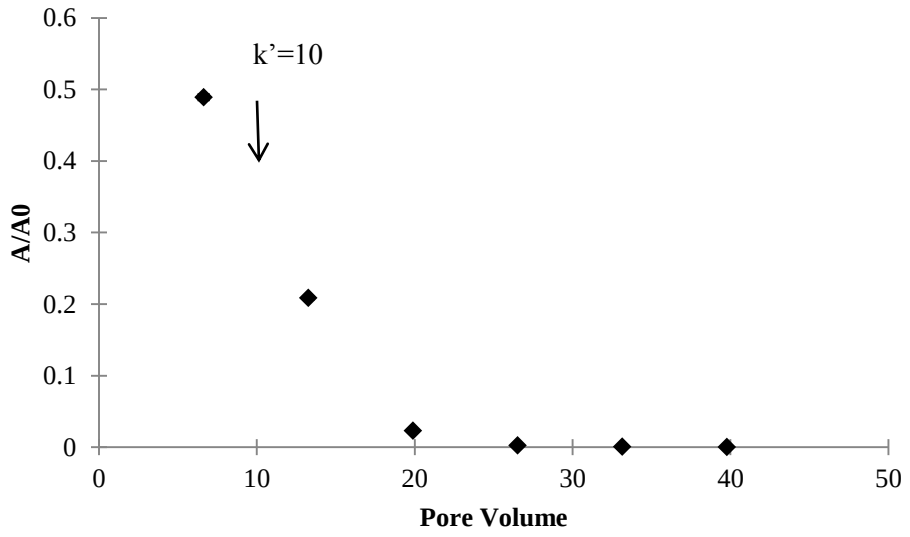


Figure 9: Activity/initial activity vs pore volume of CaF_2:Eu in 2M HCl + 0.015 M Ca^{2+} for k' determination.

5.2.2 Novel Method Column Background Count Rate and Detection Efficiency Determination

An experiment was performed to determine the background count rate for CaF_2:Eu-Pb resin mixture columns processed by the novel method, with a 12 hour count time and at least a 2 hour dark adapt (raw data found in Table A-6). The data from this experiment is presented in Table 6. Significant variation was observed in the count rate for each column in this set as the standard deviation is greater than 50% of the mean. The cause of this variation is unknown. However, a possible cause is the variation in the column efficiencies based on the mixture of the CaF_2:Eu-Pb resin columns (Table 5). The batch of the CaF_2:Eu-Pb resin mixture was the same for the background columns.

However, they were hand mixed and hand packed, which could lead to variability in the mixture and therefore the detection efficiency.

Table 6: Background determination for CaF_2:Eu-Pb resin mixture columns, based on a 12 hour count time.

Background Column	Counts	Count Rate (cpks)
1	3843	89.0
2	1578	36.5
3	4540	105.1
Mean	3320.3	76.9
Standard Deviation	1548.6	35.8

Experiments were performed to determine an expected detection efficiency for MDC calculations and to investigate the reproducibility of these measurements (raw data in Table A-4). The data for these experiments are presented in Table 7. Two independent experiments, columns 1 and 2, were performed as scoping experiments to determine the expected detection efficiency for the CaF_2:Eu-Pb resin mixture in the column geometry. Columns 3, 4, and 5 were prepared using the CaF_2:Eu-Pb resin mixture from the batch prepared for the groundwater columns. The CaF_2:Eu used in these columns was crushed and sieved separately from the CaF_2:Eu used in the scoping experiments. The detection efficiency for all five columns remained relatively constant, and no significant difference was observed between the two batches.

Table 7: Column loading and detection efficiencies for ^{210}Po spiked directly onto a conditioned column.

Column	Loading Efficiency (%)	Detection Efficiency (%)
1	100	22.7
2	100	23
3*	99.7	20.7
4*	99.7	28.4
5*	99.7	17.1
Mean	100	22.4
Standard Deviation	0.16	3.7

*From batch mixture for groundwater columns

Four spiked DDI water samples were prepared following the novel method for yield determination. The results from this study are found below in Table 8. The mean value of the yield and detection efficiency was 18.2 ± 4.6. Using the average detection efficiency 22.4% from the directly spiked columns in Table 7, the average projected yield was 81.3 ± 23.9. For column 3, the projected Y is higher than 100% which indicates the detection efficiency for this column is greater than 22.4% Based on the average yield and detection efficiency from the experiment (18.2%) and a 12 hour count time, the MDC (determined by equation 2) for the method was determined to be 53 mBq/L.

Two additional columns were prepared using a ^{210}Po spiked synthetic groundwater (Table 9). Although the yield and detection efficiency for these columns were within one standard deviation of the mean for the DDI water sample columns, the mean values were lower than the mean value obtained in the DDI water columns (raw data in Table A-8).

Table 8: Yield and detection efficiency determination for the novel method on spiked DDI water samples. Projected yield is determined assuming a detection efficiency of 22.4 % based on average detection efficiency of the spiked columns in Table 7.

Column	Activity Added (mBq)	Yε (%)	Projected Y (%)
1	4670	17.1	76.2
2	4670	13.9	61.9
3	4650	26.0	116.0
4	4620	15.9	71.1
Mean		18.2	81.3
Standard Deviation		4.6	23.9

Table 9: Yield and detection efficiency data for the novel method using spiked synthetic groundwater. Projected yield is determined assuming a detection efficiency of 22.4 % based on average detection efficiency of the spiked columns in Table 7.

Sample	Activity Added (mBq)	Yε (%)	Projected Y(%)
1	334	15.4 ± 0.6	68.8 ± 2.6
2	2300	17.2 ± 0.1	77.2 ± 0.4
Mean		16.3	72.9

5.3 Groundwater Concentration Determination

Scoping experiments were performed on each water sampling location using the method of standard additions with one spiked and one unspiked sample to determine an expected ^{210}Po concentration in the waters. The data for these experiments is found in Appendix C. All projected water sample concentrations were above the minimum detectable concentrations for the standard method of 2.0 mBq/L. The scoping experiment

results were also used to select ^{210}Po spike values for the standard additions samples used in the standard and novel method.

Groundwater concentrations were determined using the standard (raw data in Table A-9) and novel method (raw data in Table A-10). Figure 10 is an example alpha spectroscopy spectrum for the standard method and Figure 11 is an example spectrum from the Quantulus for the novel method. Both spectra are from the Nevada sampling location. Figure 12-16 contain the results for each water sampling location for both methods. Error analysis based on counting statistics has been performed, but the error is smaller than the markers used. Using the y-intercept (count rate with no activity added) from these graphs coupled with the slope (yield and detection efficiency term), ^{210}Po concentrations in each water location were determined.

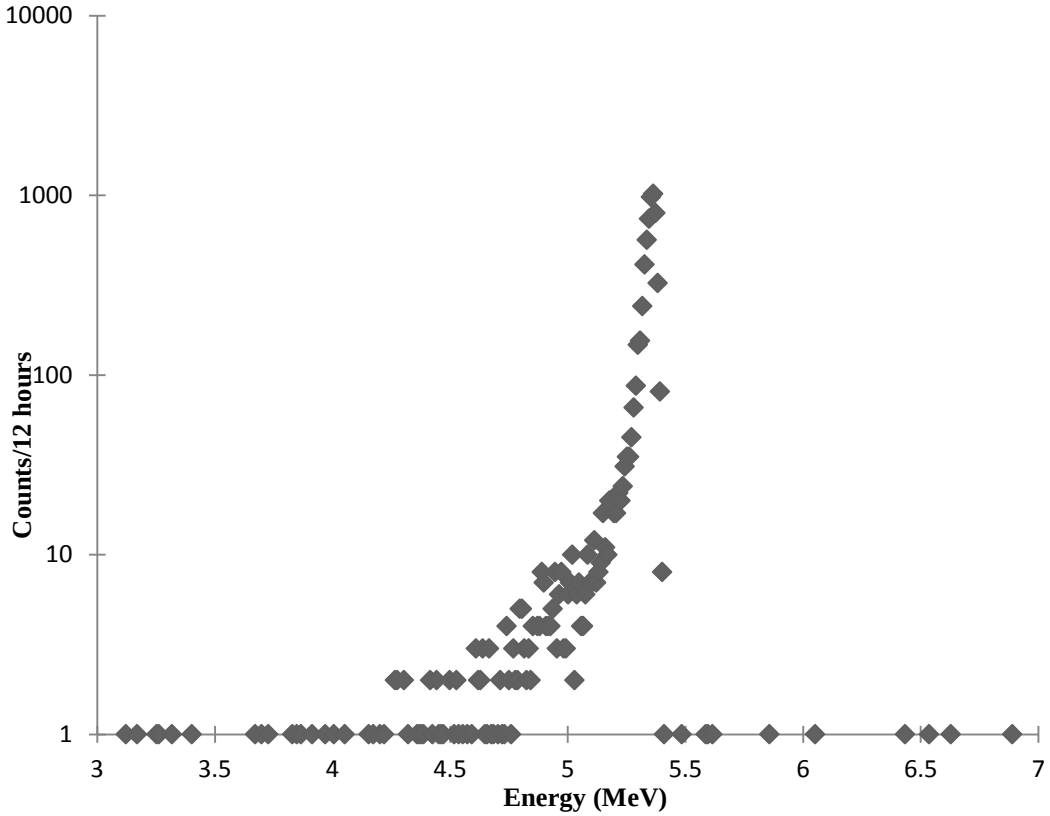


Figure 10: Spectrum from the alpha spectrometer for the unspiked Nevada sample for the standard method.

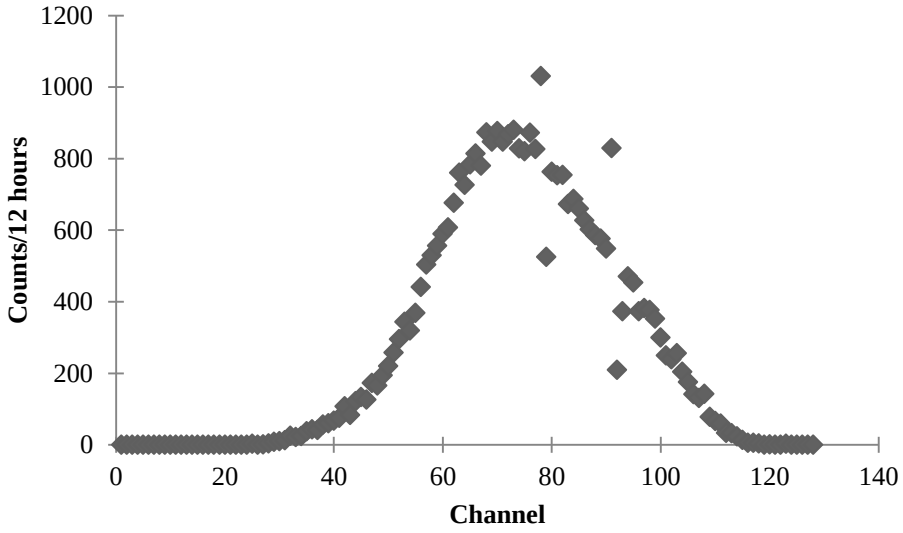


Figure 11: Spectrum from the Quantulus for the Nevada + 750 mBq sample using the novel method.

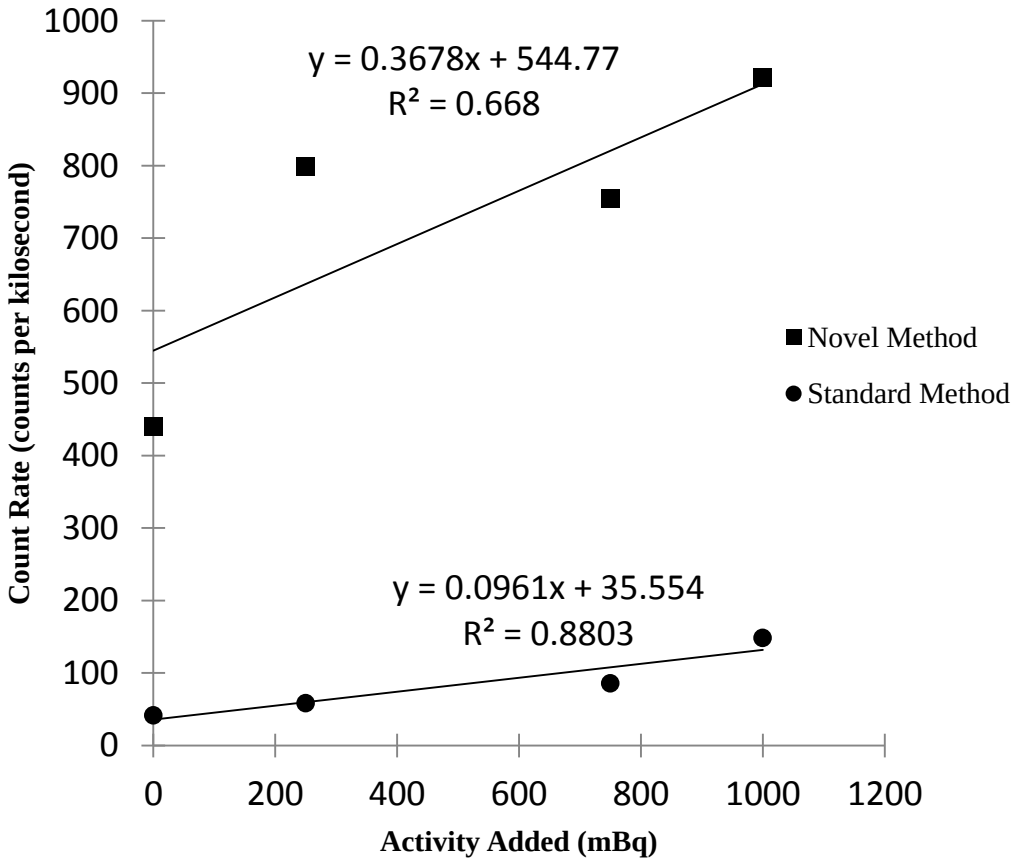


Figure 12: Standard and novel method results for Nevada groundwater. Error bars associated with counting statistics are smaller than the markers.

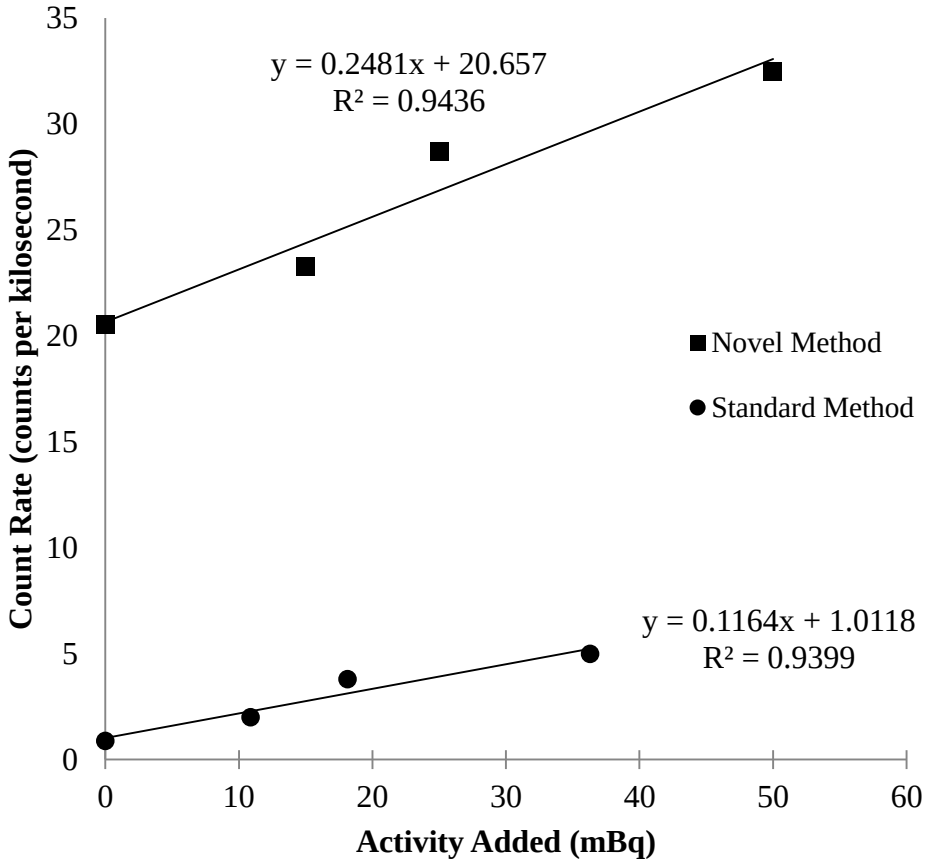


Figure 13: Standard and novel method results for Whitewater Falls. Error bars associated with counting statistics are smaller than the markers.

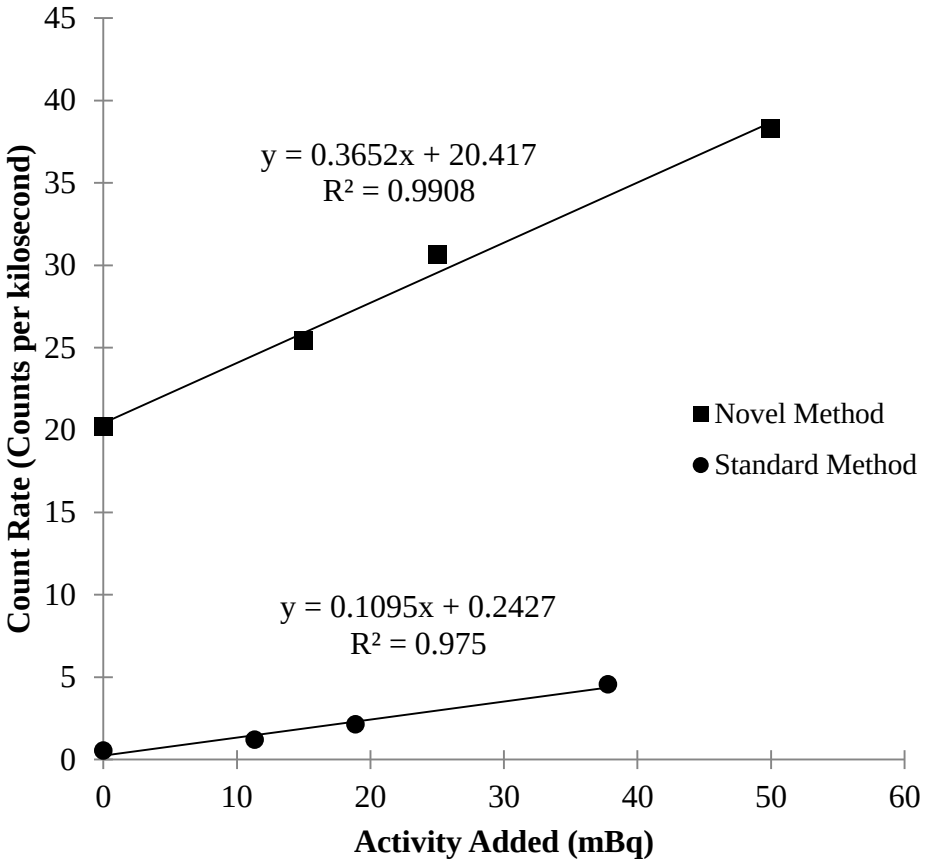


Figure 14: Standard and novel method results for Table Rock State Park. Error bars associated with counting statistics are smaller than the markers.

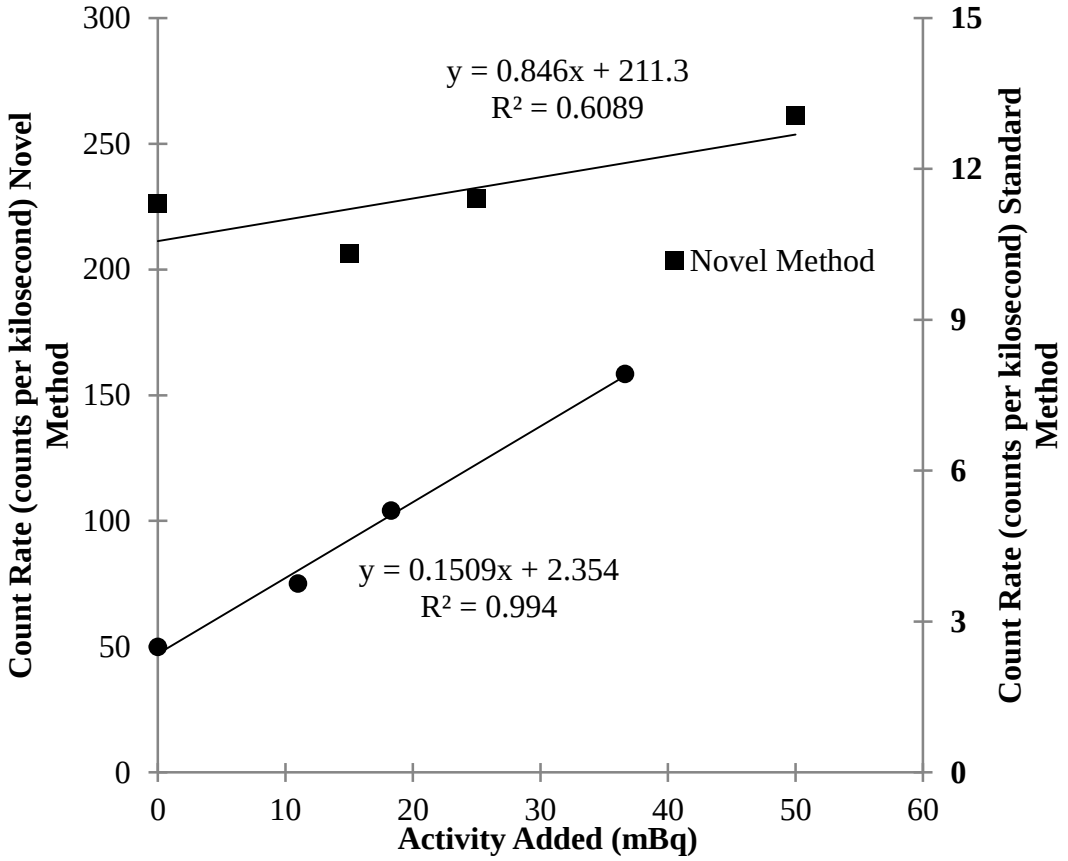


Figure 15: Standard and novel method groundwater results for Devil's Fork State Park. Error bars associated with counting statistics are smaller than the markers.

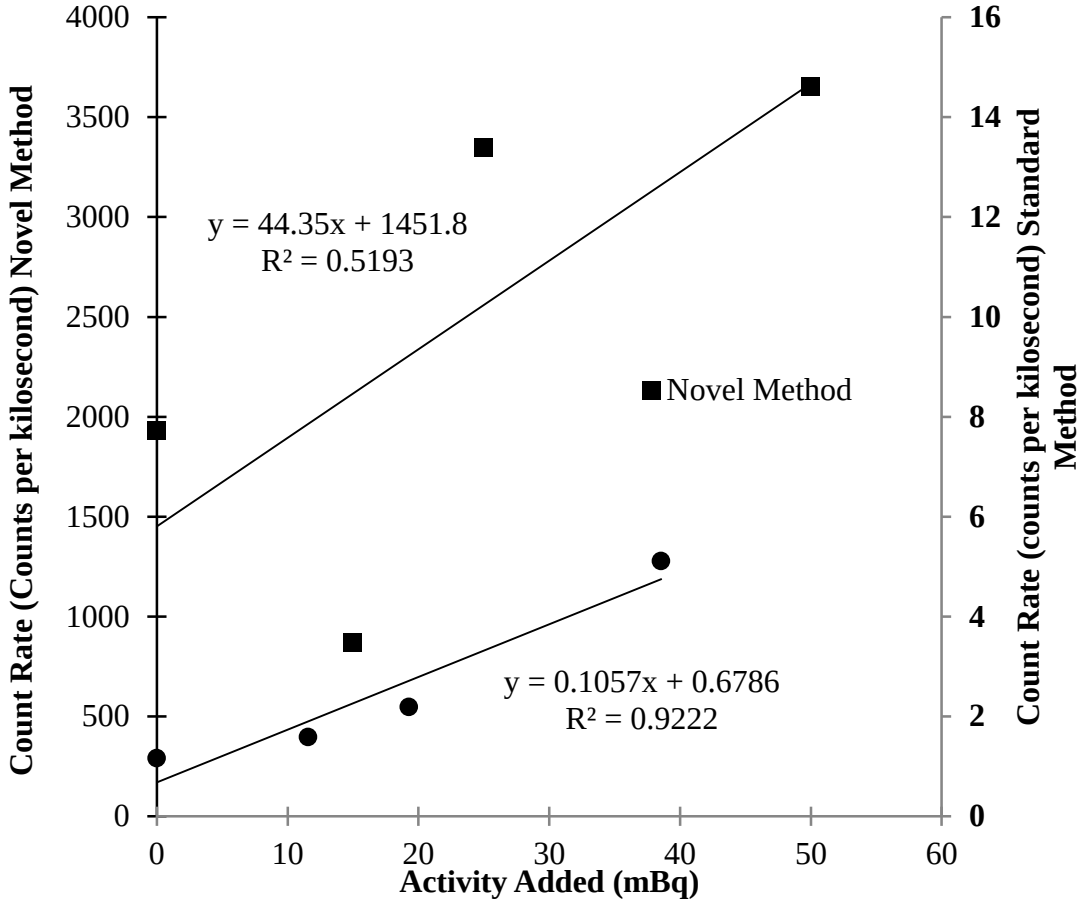


Figure 16: Standard and novel method results for Round House Point. Error bars associated with counting statistics are small than the markers.

The novel and standard method concentrations are summarized in Table 10. The concentrations were decay corrected to the time of collection without considering supported ^{210}Po. There is not good correlation between the concentrations found by the standard and novel methods. In every case where the concentration was above the minimum detectable concentration, the concentration determined by the novel method trended higher, ranging from 37.2% higher for the Nevada sampling site to 90.3% higher for Devil's Fork State Park, compared to the concentration determined by the standard method. Due to the high and variable background (Table 6) there is significant

uncertainty in the concentrations determined by the novel method. The water from the Nevada sampling location was also analyzed by the EPA in Nevada, and they reported a concentration of 3,030 ± 132 mBq/L, which is 30% higher than the concentration measured by the standard method and 18% lower than the concentration measured by the novel method.

Table 10: Comparison of standard and novel method groundwater concentrations

	Standard Concentration (mBq/L)	Novel Concentration (mBq/L)	Difference (%)
Nevada	2324.9 ± 94.5	3703 ± 285.9	37.2
White Water Falls	58.1 ± 3.41	<MDC[1] [3]	---
Table Rock State Park	57.6 ± 20.06	<MDC[2] [3]	---
Devil's Fork State Park	97.21 ± 4.42	1003.05 ± 1389.8	90.3
Round House Point	18.16 ± 1.56	91.59 ± 6.91	80.2

[1] Falls Novel Method Concentration= -1427.71 ± 914.32

[2] Table Rock State Park Novel Method Concentration=-456.1 ± 573.13

[3] Concentrations > MDC at time of collection, but decayed to <MDC at the time of analysis (Table A-11)

The ^{210}Po in the water at the Nevada sampling site is known to be unsupported ^{210}Po based on very low levels of ^{210}Pb in the water [Seiler, 2010]. Whitewater Falls and Devil's Fork State Park samples were collected 4 months before Round House Point and Table Rock state park were collected and 5 months before the Nevada water was collected. In addition to the difference in collection times, the standard method samples were processed 1 month before the novel method samples. The ^{210}Po from the sampling locations other than Nevada may be supported or unsupported, which may cause issues in the comparison of the two sets of data. If the ^{210}Po is supported, the difference in the

time of collection and analysis may skew the data as ^{210}Po ingrowth has not been considered in the concentration determination. If this ingrowth is occurring, the samples with the longest time between collection and processing may yield artificially high concentrations. If the ^{210}Po is unsupported, which is the assumption, the difference in collection and processing time will not affect the measured concentrations as the concentrations are being decay corrected to the time of collection. These conditions should have been more closely monitored to reduce the variables between the methods. There appears to be other factors, in addition to the issues associated with the variation in collection and processing times and the supported versus unsupported ^{210}Po, affecting the novel method concentrations. The water collected from the Nevada site was known to have unsupported ^{210}Po, but the concentration determined by the novel method is still 37.2% different from the standard method activity.

The data from the Round House Point and Devil's Fork State Park sampling locations (Figure 15 and Figure 16), have the greatest variation between the standard and novel methods. As the count rate for these two novel method sets was so high compared to the expected ^{210}Po activity on the column, a radiological interferent was suspected. As these waters are known to have very high U concentrations (EE&S 813, 2008), U or its progeny were thought to be likely interferents. In an attempt to determine the interferent(s) and the amount of ^{210}Po on the novel method columns, one of the spiked columns from each water sample location was eluted with 6M HNO_3. The eluent was then evaporated onto a planchet for analysis by alpha spectroscopy.

The alpha spectra from these elutions are below in Figure 17 and Figure 18 and demonstrate that ^{238}U (4.196 MeV) and ^{234}U (4.775 MeV) were eluted from the columns in addition to the ^{210}Po. There was significant tailing on each alpha peak due to salt formation from the evaporation of the 6M HNO_3 making quantification of activity from each individual uranium peak problematic. The tailing also makes it impossible to resolve the ^{235}U peak, however, due to natural isotopic ratios, it is assumed to be present as well. To quantify the activity from uranium (^{238}U, ^{235}U, and ^{234}U), the count rate from the entire alpha spectrum up to 4.775 MeV was used. The total U concentration (mBq/L) on the columns was calculated based on activity ratio of ^{238}U and ^{234}U from alpha spectroscopy of Round House Point column elution, and the typical isotopic abundance of ^{235}U. The estimated activity for the total U from each column assuming 50% of the U from the aqueous was removed (discussion on 50% removal on pp. 56 and 57) the column and 100% of the U was eluted from the columns is in Table 11.

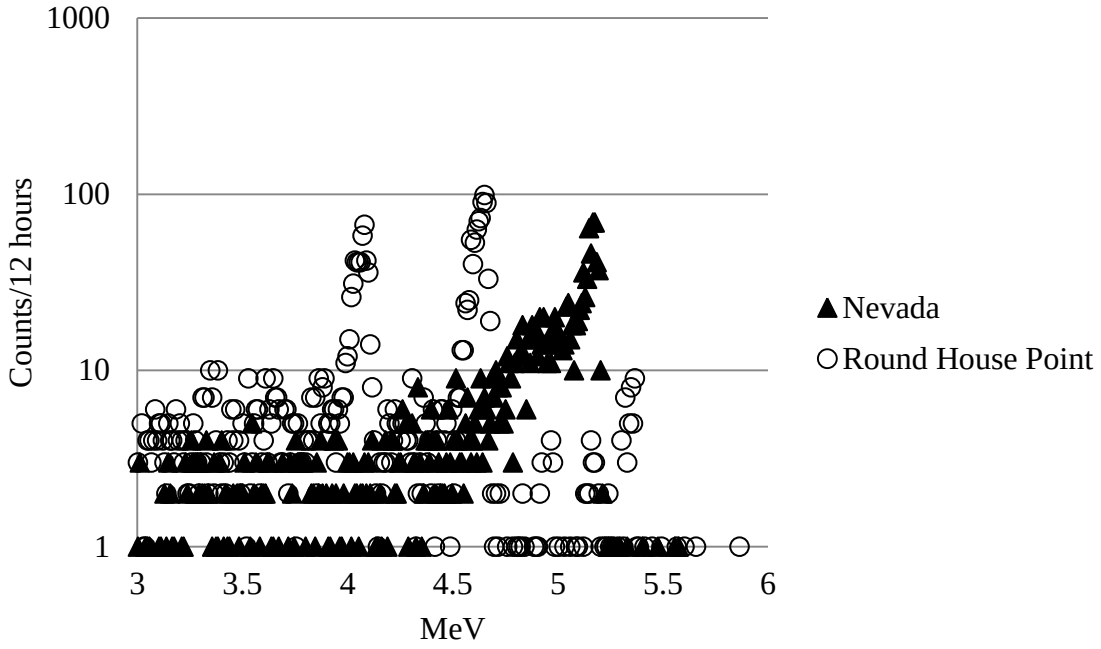


Figure 17: Alpha spectroscopy spectra from column elutions for Round House Point and Nevada sampling locations.

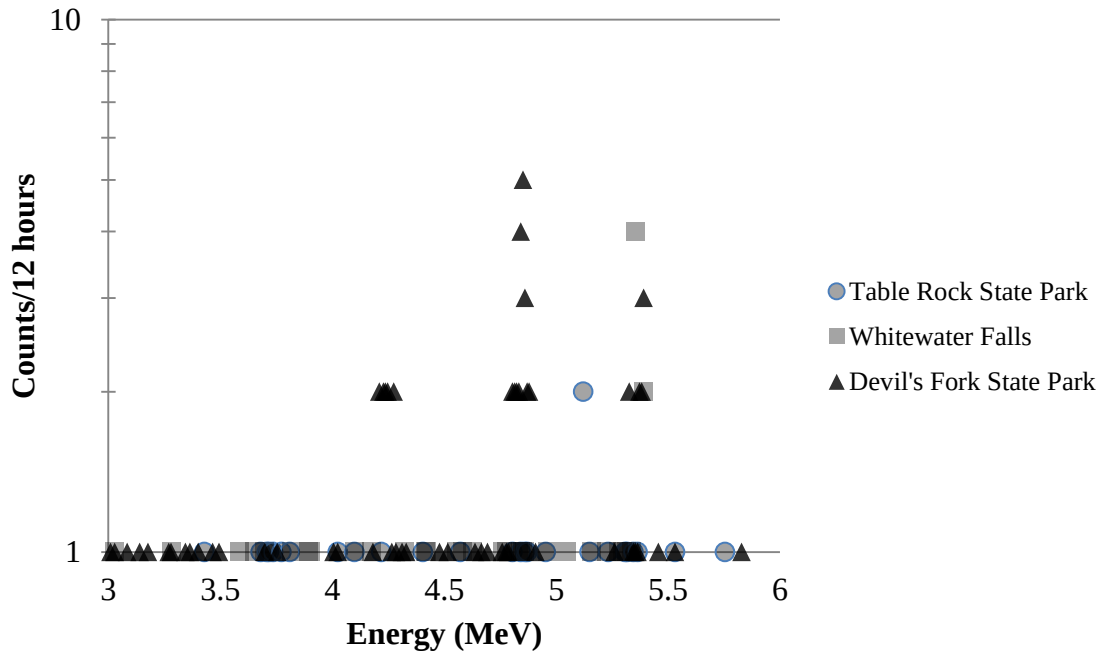


Figure 18: Alpha spectroscopy spectra from column elutions for Table Rock State Park, Whitewater Falls, and Devil's Fork State Park.

Uranium-238 analysis for each water sample was performed on the ICP-MS. The raw data (µg/L) is found in Table A-14. This value was used to determine total U concentration (mBq/L) found in Table 11. As expected based on previous studies (EE&S 813, 2008), Round House Point and Devil's Fork State Park had high levels of U. Gross alpha measurements by LSC (Table 11) were also performed for each water sample location (raw data in Table A-13). This data corresponds well to the abnormally high count rates seen on these sample analyses. It appears that the retention of U on most of the analyses may be at least partially responsible for the high trending concentration results. The time between collection and sample processing was different for these measurements compared to the processing of the standard and novel method

concentration determination. However, the two locations with the greatest discrepancy between the count rates and the expected ^{210}Po activity on the columns Round House Point and Devil's Fork State Park), both also have high gross alpha concentrations compared to the expected ^{210}Po activity.

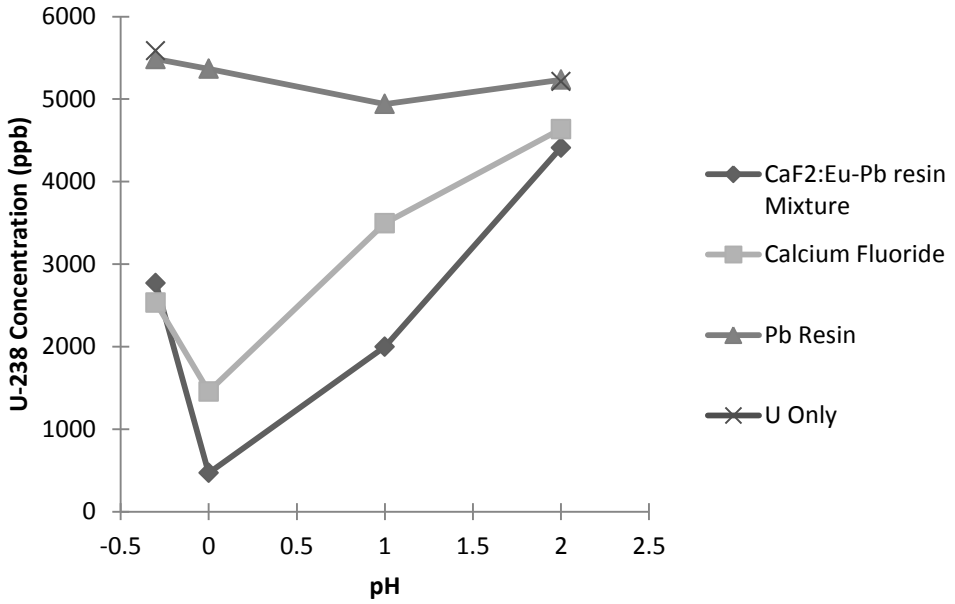
Table 11: Total U concentration (mBq/L) as determined by ICP-MS, projected U Activity retained on CaF_2:Eu-Pb resin columns assuming 50% removal from the aqueous phase and 0.5L sample volume, total U activity (mBq) eluted from CaF_2:Eu-Pb resin columns as measured by alpha spectroscopy, and gross alpha concentration (mBq/L) as determined by LSC.

	Total Aqueous U Concentration (mBq/L) (based on ICP-MS)	Projected U Activity on CaF_2:Eu-Pb Resin Columns (mBq)	Total U Activity Eluted (mBq) (Alpha Spec)	Gross Alpha Concentration (mBq/L) (LSC)
Nevada	8.97± 0.02	2.22	--	626.36 ± 67.75
Whitewater Falls	6.91 ± 0.04	1.71	3.06	54.27 ± 62.65
Table Rock State Park	17.30± 0.15	4.29	3.59	26.357 ± 62.39
Devil's Fork State Park	334.61 ± 0.57	82.98	25.53	501.94 ± 66.67
Round House Point	10002.0 ± 20	2480.50	591.41	11072.9 ± 129.39

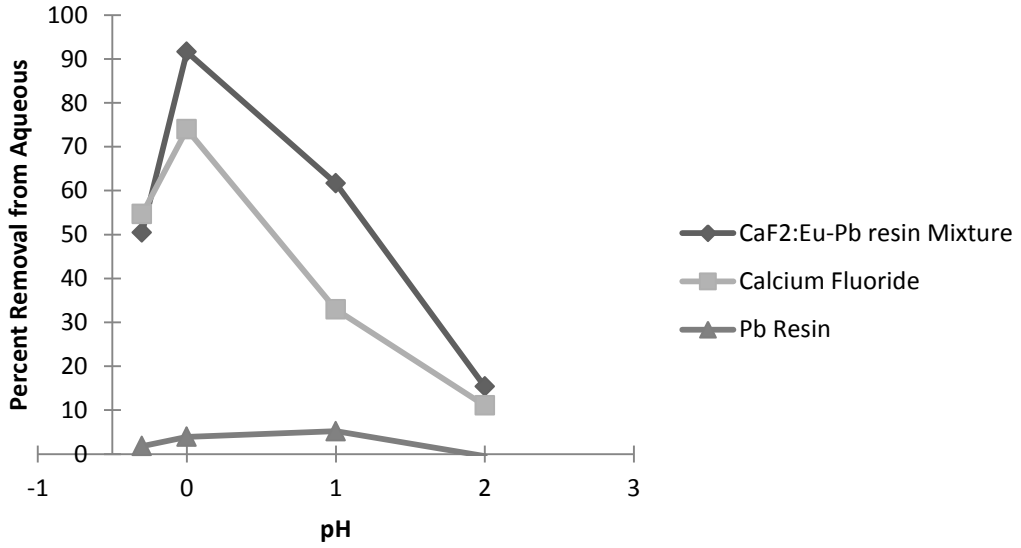
Uranium remaining on the columns was a surprise based on the published data for the extraction chromatography resin and CaF_2:Eu regarding U. Uranium should not have had been retained by an 18-crown-6 ether on the resin in 2M HCl [Yakshin et al., 2009]. Studies on U and CaF_2:Eu, although shown to retain U in higher pH systems, found that U sorption decreased with decreasing pH down to pH 2 [DeVol et al., 1996]. As the addition of the Ca^{2+} had an effect on the retention of Po on the Pb resin, it was thought

that possibly it was affecting the retention of U as well. A batch uptake uranium removal experiment was performed on the ICP-MS for 0.01M HCl + 7.5 x 10^{-5} M Ca^{2+}, 0.1M HCl + 7.5 x 10^{-4} M Ca^{2+}, 1M HCl + 7.5 x 10^{-3} M Ca^{2+}, and 2M HCl + 1.5 x 10^{-2} M Ca^{2+} to determine if U was removed from the aqueous phase and which constituent was responsible for removal (raw data found in Table A-12). The data from this experiment is found in 19a and 19b. The U only points were the control samples that did not contain other media than the HCl and Ca^{2+} solutions and U spike. Based on this experiment, the assumption on the Pb resin was correct; U did not have an affinity for the Pb resin in any of the acid conditions. However, around half of the U in the solution was removed from the aqueous phase for the CaF_2:Eu and the CaF_2:Eu-Pb resin mixture in the 2 M HCl + 0.015M Ca^{2+} (Figure 19b). The mechanism for the removal of the U from the aqueous phase is not known, but does supports the data found with the resin sample analyses. Assuming the column arrangement of the CaF_2:Eu-Pb resin mixture columns removed the same percentage as the batch uptake experiment in 2M HCl (49.6% compared to the uranium control, Figure 19a and 19b) the projected uranium activity in a 500 mL sample is given in Table 11. For the two locations with low U concentrations, Whitewater Falls and Table Rock State Park, the eluted activities are consistent with the expected activities on the column. However, for the two locations with higher levels of U, the activity eluted from the column is much lower than the expected activity on the column. There are two possible reasons for this discrepancy. Although the U sorption experiment was designed to mimic the conditions of the novel method columns, the CaF_2:Eu-Pb resin mixture had contact with all the aqueous phase for 45 minutes. This time frame is similar

to the total amount of the time the CaF_2:Eu-Pb resin mixture was being contacted in the columns, however, the contact in the columns was in a small volume with a constant flow rate. This could be responsible for less removal from the aqueous phase than expected. Also, the elution technique used to remove the U from the column was the technique to remove ^{210}Po. Although it does appear that the 6M HNO_3 facilitated removal U from the column, the amount is unknown. Due to some dissolution of the CaF_2:Eu in the 6M HNO_3, the columns could not be recounted on the liquid scintillation counter using the current geometry. Total dissolution of the CaF_2:Eu, removal of the Pb resin from the column, and mixing the two with liquid scintillation cocktail in traditional liquid scintillation vials could have facilitated recounting of the samples, but this was overlooked.



(a)



(b)

Figure 19 (a): Uranium concentration in the aqueous phase after the batch uptake experiments for CaF_2:Eu, Pb resin, and the CaF_2:Eu-Pb resin mixture used in column experiments. (b): Percent Uranium removal from the aqueous phase following batch uptake experiments, based on the concentration remaining the aqueous phase less the concentration remaining in the U blanks aqueous phase

5.4 Future Work

A variety of other possible novel ^{210}Po methods were investigated before selecting the mixed bed extraction chromatography-scintillator resin mixture. Although not selected for this work, many of these methods showed promising preliminary results. The most promising of these methods was likely the homogeneous Pb extraction chromatography resin. The preliminary results for this study yielded excellent results (yields around 100% for DDI water samples). The use of the homogenous resin would eliminate the U interference seen with the CaF_2:Eu, as the granulated scintillator would not be necessary, and would eliminate variation in the detection efficiency based on mixing of the resin and CaF_2:Eu. Unfortunately, as this resin was specially developed by Eichrom Technologies, Inc., more definitive results may be necessary before the resin could be reproduced.

ZnS:Ag disks also should promising results for ^{210}Po detection (Appendix C). The method using spontaneous deposition onto ZnS:Ag was based on ^{210}Po deposition onto the Ag used to dope the ZnS. This process is most effective at low pHs, however, in these harsh conditions, ZnS:Ag disks begin to dissolve. Although yields around 60% were obtained in pH 5 spiked DDI solutions, the mechanism for deposition onto the disks was not known, as these conditions are not favorable to spontaneous deposition on silver. The selectivity of the method for ^{210}Po was also in question as the deposition mechanism was unknown. Additional studies on the mechanism for deposition are necessary to determine if this method could be a viable option for ^{210}Po determination.

Another method that has not yet been investigated is the use of a Ag nanoparticle-plastic scintillating bead matrix. Using the standard method spontaneous deposition conditions, heated acidic solutions, ^{210}Po could be isolated by spontaneous deposition onto the Ag nanoparticles. By optimizing the flow rate through the matrix, this method could possibly be used without a pre-concentration. As polonium is unique in that it spontaneously sticks to a variety of metals, this method would be selective for polonium, and may also cut down on polonium losses due to resin breakthrough.

CHAPTER FIVE

CONCLUSIONS

A novel method was investigated for the quantification of ^{210}Po in water as an alternative to the standard method of spontaneous plating onto Ag disks followed by quantification with an alpha spectrometer. The novel method utilized a column containing a 50:50 by volume mixture of Pb resin (Eichrom Technologies, Inc.) mixed with granulated CaF_2:Eu scintillator. ^{210}Po was concentrated from a 0.5 L sample by MnO_2 co-precipitation. Following purification on the column and prior to elution, ^{210}Po was quantified on a liquid scintillation counter without the introduction of liquid scintillation cocktail. The average detection efficiency for spiked columns was 22.4 ± 3.67%. The average Yε was 18.2 ± 4.64% for the CaF_2:Eu-Pb resin mixture columns using spiked DDI water and 16.3% for spiked synthetic ground water samples. The minimum detectable concentration for the novel method is 53 mBq/L based on a 12 hour count time and an average background count rate of 0.07 ± 0.04 cps.

^{210}Po concentrations were determined for five groundwaters from locations in upstate region of South Carolina and Nevada. Novel method determined concentrations ranged from <MDC to 3703.0 mBq/L compared to Standard method concentrations of 18.2 to 2324.9 mBq/L. Correlation between the concentrations found by the standard and novel methods was not good. In every case where the concentration was above the MDC for both methods, the concentration determined by the novel method trended higher, ranging from 37.2% to 90.3 %, compared to the concentration determined by the standard method.

Uranium isotopes were found to concentrate on the columns used in the novel method and acted as a radiological interferent. The retention of U by the column was surprising based on data in the literature regarding previous uptake studies the Pb extraction chromatography resin and CaF_2:Eu. A batch uptake experiment was performed for the Pb resin, CaF_2:Eu, and the CaF_2:Eu-Pb resin mixture, and it was determined that the CaF_2 mixture removed close to 50% of U from the aqueous phase, although the mechanism for removal is unknown.

Good results were obtained in spiked DDI and synthetic groundwater. With an MDC of 53 mBq/L, the method does meet the desired objective of 100 mBq/L, the limit set by the World Health Organization. However, the MDC is much higher than that of the standard method (2 mBq/L) for the same sample volume and count time, and due to high variability in the background for the novel method columns, there is significant uncertainty in the concentrations determined by this method. Also, with the selection of CaF_2:Eu as the granulated scintillator for the novel method columns, the method is subject to interferences from U. The novel method developed in this study is not a good method for ^{210}Po determination in groundwater.

Appendix A: Results and Discussion Supporting Data

Table A-1 Standard method spike test yield determination supporting data (pH 1, 80°C, 3.85E-05 (cps) background)

Count Rate Sample (cps)	ε (%)
4.80 E-02	6.32
1.38 E-01	17.6
9.51 E-02	17.6
4.80 E-02	6.32

Table A-2 Standard method groundwater yield determination supporting data (3.85E-05 (cps) background)

Location	Count Rate Unspiked Sample (cps)	Count Rate Spiked Sample (cps)	Activity Added (Bq)	ε (%)
A Bottle 1	7.57E-04	1.07E-02	0.032	5.92
A Bottle 2	6.76E-04	7.78E-02	0.0216	6.32
A Bottle 2	5.00E-04	6.61E-03	0.02	5.92
A Bottle 3	3.76E-02	8.90E-02	0.0371	5.92
B	1.14E-03	3.03E-02	0.056	6.32
B	7.84E-04	3.51E-02	0.0278	5.92
C	1.94E-02	9.46E-04	0.0259	5.92

Table A-3 Detection efficiency determination of CaF_2:Eu-Pb resin mixture supporting data (0.003 (cps) background)

CaF_2:Eu-Pb Resin Ratio	Count Rate (cps)	Activity Added (Bq)	Load Count Rate (cps)	Load Background Count Rate (cps)
60-40	1.19	3.74	0.016	0.006
70-30	1.21	3.79	0.014	0.006
80-20	1.93	3.68	0.018	0.006

Table A-4 50:50 CaF_2:Eu-Pb resin detection efficiency determination supporting data (count time = 18000s, background counts = 826, background count time =172800s)

Column	Counts	Activity Added (Bq)
1	20116	5.47
2	24075	5.74
3	20985	5.61
4	29429	5.76
5	17914	5.79

Table A-5a Supporting Data for k' for Pb resin with 2M HCl (Pb resin weight = 0.272, background counts = 6, count time = 1800s)

Elution Volume (mL)	Activity Added (Bq)	Elution Counts
2.00	5.70	13
4.00	5.70	11
6.00	5.70	3
8.00	5.70	55
10.00	5.70	251
12.00	5.70	374
14.00	5.70	361
16.00	5.70	470
18.00	5.70	452
20.00	5.70	477
22.00	5.70	429
24.00	5.70	297
26.00	5.70	360
28.00	5.70	346
30.00	5.70	339
32.00	5.70	347
34.00	5.70	233
36.00	5.70	315
38.00	5.70	393
40.00	5.70	276
42.00	5.70	237
44.00	5.70	247
46.00	5.70	261
48.00	5.70	234
50.00	5.70	211

Table A-5b Supporting Data for k' for Pb resin with 2M HCl (Pb resin weight = 0.7g, background counts = 85, Activity Added = 10.57 Bq, count time = 7200s)

Elution Volume (mL)	Effluent Counts
10	< bknd
20	< bknd
30	< bknd
40	< bknd
50	< bknd
60	48
70	36
80	82
90	108
100	164
110	249
120	381
130	877
140	1020
150	1227
160	1306
170	1216
180	1193
190	1135
200	1064
210	889

Table A-5c: Supporting Data for k' for Pb resin with 2M HCl + 0.015M Ca^{2}+ (Pb resin weight = 0.305g, activity added = 4.95 Bq, background counts = 6, count time = 1800s)

Elution Volume (mL)	Elution Counts
3.00	7
6.00	11
9.00	43
12.00	69
15.00	100
18.00	155
21.00	201
24.00	238
27.00	333
30.00	480
33.00	484
36.00	522
39.00	496
42.00	432
45.00	397
48.00	360
51.00	349
54.00	287
57.00	265
60.00	254
63.00	215
66.00	206
69.00	193
72.00	207
75.00	183
78.00	151
81.00	129
84.00	96
87.00	75
90.00	76

Table A-5d: Supporting Data for k' for CaF_2:Eu-Pb Resin (CaF_2:Eu-Pb resin weight = 0.29, activity added = 2.619 Bq, background counts = 6, count time = 1800s)

Elution Volume (mL)	Effluent Counts
3.00	53
6.00	145
9.00	277
12.00	336
15.00	316
18.00	298
21.00	289
24.00	247
27.00	210
30.00	169
33.00	168
36.00	125
39.00	135
42.00	114
45.00	98
48.00	91

Table A-5e: Supporting Data for k' for CaF_2:Eu (CaF_2:Eu weight = 1.12g, activity added = 7.4 Bq, background counts = 12, count time = 3600s)

Elution Volume (mL)	Effluent Counts
1	13047
2	5569
3	629
4	80
5	36
6	15

Table A-6 CaF_2:Eu-Pb Resin Novel Method Background Determination Supporting Data (count time = 43,200s)

Background	Counts
1	3483
2	1587
3	4540

Table A-7 Yield and Efficiency Determination for the Novel Method in DDI Water Supporting Data (activity added = 4.67Bq, background count rate = 0.08 cps, count time = 36000s)

Column	Counts
1	29127
2	25236
3	44538
4	27179

Table A-8 Yield and Efficiency Determination for the Novel Method in Synthetic Groundwater Supporting Data (background count rate = 0.08 cps, count time = 43200s)

Column	Counts	Activity Added (Bq)
1	910	0.0184
2	897	0.031
3	1053	0.042
4	2243	0.055
5	5428	0.334
6	20365	2.3

Table A-9 Standard Method Groundwater Raw Data (count time = 172000s, background count rate = 0.029 cpks)

Location	A_{decay} Corrected Added (mBq)	Count Rate (cpks)
Nevada 1	0	41.8
Nevada 2	250	58.5
Nevada 3	750	86.0
Nevada 4	1000	148.3
White Water Falls 1	0	0.8
White Water Falls 2	10.89	2.0
White Water Falls 3	18.15	3.8
White Water Falls 4	36.3	5.0
Table Rock State Park 1	0	0.5
Table Rock State Park 2	11.34	1.2
Table Rock State Park 3	18.9	2.1
Table Rock State Park 4	37.8	4.5
Devi's Fork State Park 1	0	2.5
Devil's Fork State Park 2	11	3.7
Devil's Fork State Park 3	18.3	5.2
Devil's Fork State Park 4	36.65	7.9
Round House Point 1	0	1.2
Round House Point 2	11.57	1.6
Round House Point 3	19.275	2.2
Round House Point 4	38.55	5.1

Table A-10 Novel Method Groundwater Raw Data (count time = 43,200s, background count rate = 76.8 cpks)

Sample Location	Activity Added (mBq)	Count Rate (cpks)
Nevada 1	0	439.3
Nevada 2	250	799.4
Nevada 3	750	754.6
Nevada 4	1000	921.4
White Water Falls 1	0	20.5
White Water Falls 2	15	23.3
White Water Falls 3	25	28.7
White Water Falls 4	50	32.5
Table Rock State Park 1	0	20.2
Table Rock State Park 2	15	25.4
Table Rock State Park 3	25	30.6
Table Rock State Park 4	50	38.3
Devil's Fork State Park 1	0	225.9
Devil's Fork State Park 2	15	206.1
Devil's Fork State Park 3	25	228.2
Devil's Fork State Park 4	50	261.1
Round House Point 1	0	1933.2
Round House Point 2	15	867.4
Round House Point 3	25	3347.3
Round House Point 4	50	3650.9

Table A-11: Comparison of standard and novel method groundwater concentrations

	Standard Concentration (mBq/L)	Novel Concentration (mBq/L)	Standard Concentration Decay Corrected (mBq/L)	Novel Concentration Decay Corrected (mBq/L)	Difference (%)
Nevada	739.32 ± 30.05	2544.7 ± 196.45	2324.9 ± 94.5	3703 ± 285.9	37.2
White Water Falls	18.42 ± 1.08	<MDC[1]	58.1 ± 3.41	<MDC[1]	---
Table Rock State Park	39.02 ± 13.58	<MDC[2]	57.6 ± 20.06	<MDC[2]	---
Devil's Fork State Park	30.82 ± 1.4	317.97 ± 440.58	97.21 ± 4.42	1003.05 ± 1389.8	90.3
Round House Point	12.3 ± 1.06	62.01 ± 4.68	18.16 ± 1.56	91.59 ± 6.91	80.2

[1] White Water Falls Novel Concentration = -452.78 ± 289.84; Whitewater Falls Novel Method Decay Corrected Concentration= -1427.71 ± 914.32

[2] Table Rock State Park Novel Concentration=-308.78 ± 388.01; Table Rock State Park Novel Method Decay Corrected Concentration=-456.1 ± 573.13

In Table A-11 columns 2 and 3 concentrations were determined without decay correction, although the ^{210}Po spike activity was decay corrected to account for the time between the spiking of the groundwater samples at the beginning of the standard method sample preparation and actual counting on the alpha spectrometer. The concentrations in columns 4 and 5 were decay corrected to the time of collection without considering supported ^{210}Po.

Table A-12 Raw Data from U removal experiment

	Sample		Uranium (ppb)	% RSD	Error (ppb)
1	Sample	11/15/2010 4:40:19 PM	0.122	18.61	0.0227042
2	Standard 1	11/15/2010 4:44:51 PM	0.653	13.5	0.088155
3	Standard 2	11/15/2010 4:49:24 PM	0.044	4.549	0.00200156
4	Standard 3	11/15/2010 4:53:58 PM	0.068	1.923	0.00130764
5	Standard 4	11/15/2010 4:58:31 PM	0.32	0.679	0.0021728
6	Standard 5	11/15/2010 5:03:05 PM	0.644	0.108	0.00069552
7	Standard 6	11/15/2010 5:07:39 PM	1.556	0.392	0.00609952
8	Standard 7	11/15/2010 5:12:13 PM	3.19	0.228	0.0072732
9	Standard 8	11/15/2010 5:16:49 PM	6.431	1.137	0.07312047
10	Standard 9	11/15/2010 5:21:24 PM	51.5	0.489	0.251835
11	Wash Sample	11/15/2010 5:25:57 PM	0.082	3.236	0.00265352
12	2M 50/50	11/15/2010 5:32:59 PM	2770	0.514	14.2378
13	2M CaF	11/15/2010 5:37:32 PM	2533	0.476	12.05708
14	2M Pb	11/15/2010 5:42:06 PM	5485	0.338	18.5393
15	2M U	11/15/2010 5:46:40 PM	5585	0.135	7.53975
16	1M 50/50	11/15/2010 5:51:14 PM	468.6	0.062	0.290532
17	1M CaF	11/15/2010 5:55:47 PM	1455	0.22	3.201
18	1M Pb	11/15/2010 6:00:20 PM	5366	0.611	32.78626
19	Standard 5	11/15/2010 6:04:54 PM	0.678	0.75	0.005085
20	Wash	11/15/2010 6:09:28 PM	0.079	1.384	0.00109336
21	0.1M 50/50	11/15/2010 6:14:01 PM	1999	0.192	3.83808
22	0.1M CaF	11/15/2010 6:18:35 PM	3495	0.514	17.9643
23	0.1M Pb	11/15/2010 6:23:09 PM	4941	0.688	33.99408
24	0.01M 50/50	11/15/2010 6:27:43 PM	4411	0.798	35.19978
25	0.01M CaF	11/15/2010 6:32:16 PM	4635	0.444	20.5794
26	0.01M Pb	11/15/2010 6:36:51 PM	5235	0.494	25.8609
27	0.01M U	11/15/2010 6:41:25 PM	5211	0.735	38.30085
28	Standard 7	11/15/2010 6:45:59 PM	3.372	0.298	0.01004856
29	Wash	11/15/2010 6:50:33 PM	0.121	4.387	0.00530827

Table A-13 Gross alpha concentration determination by LSC raw data (count time = 172000, background = 144 counts, background count time = 43200s)

	Counts
Whitewater Falls	620
Table Rock State Park	596
Devil's Fork State Park	1005
Round House Point	10096
Nevada	1112

Table A-14 Raw Data from ^{238}U concentration in groundwater using ICP-MS determination.

			U(ppb)	%RSD
1	Sample	9/15/2010 5:29:01 PM	0	0
2	Standard 1	9/15/2010 5:33:02 PM	0.024	1.164
3	Standard 2	9/15/2010 5:37:03 PM	0.052	3.519
4	Standard 3	9/15/2010 5:41:05 PM	0.101	2.275
5	Standard 4	9/15/2010 5:45:06 PM	0.532	0.683
6	Standard 5	9/15/2010 5:49:09 PM	1.076	0.59
7	Standard 6	9/15/2010 5:53:11 PM	2.641	0.505
8	Standard 7	9/15/2010 5:57:14 PM	5.447	0.224
9	Standard 8	9/15/2010 6:01:17 PM	10.38	0.115
10	Standard 9	9/15/2010 6:05:20 PM	50.42	1.696
11	Wash Sample	9/15/2010 6:09:22 PM	0.002	70.03
12	RHP	9/15/2010 6:13:25 PM		2.292
13	TRSP	9/15/2010 6:17:26 PM		0.45
14	DFSP	9/15/2010 6:21:27 PM	10.89	0.242
15	WWF	9/15/2010 6:25:29 PM	0.224	0.997
16	NV	9/15/2010 6:29:30 PM	0.29	0.452
17	RHP Redo	9/15/2010 6:33:32 PM	330.7	0.28
18	TRSP Redo	9/15/2010 6:37:33 PM	0.973	0.677
19	Standard 4	9/15/2010 6:41:33 PM	0.548	1.024
20	Wash	9/15/2010 6:45:35 PM	0.008	71.58
21	RHP	9/15/2010 6:49:36 PM	334	0.584
22	RHP	9/15/2010 6:53:38 PM	336.1	0.134
23	TRSP	9/15/2010 6:57:39 PM	0.971	0.831
24	RHP HNO3	9/15/2010 7:01:41 PM	326.6	0.03
25	RHP Diluted HNO3	9/15/2010 7:05:42 PM	16.88	0.292
26	TRSP HNO3	9/15/2010 7:09:41 PM	0.976	0.265
27	DFSP HNO3	9/15/2010 7:13:43 PM	10.63	0.422
28	WWF HNO3	9/15/2010 7:17:44 PM	0.266	0.237
29	NV HNO3	9/15/2010 7:21:46 PM	0.307	0.61
30	Wash	9/15/2010 7:25:47 PM	0.003	77.99

Appendix B- Supplemental Data

B-1 Additional k' experiments

A variety of k' experiments were performed for Sr and Pb resin. Differences were seen based on the size of tubing although the calculations were based on pore volumes. These differences can be observed below in Tables B-1 through B-4 and Figures B-1 through B-4. Changes were also seen when there was a stop in flow. An example of this can be seen in Figure B-1. At 130 pore volumes there is a large increase in A/A_0 due to stoppage of flow.

Table B-1: Raw data for k' of Sr resin in 2M HCl in 5 mm diameter Teflon tubing (background = 12 counts)

	A/A_o	Pore Volumes	$\sigma_{A/A0}$	Count Time (s)	Counts
1.00	0.01	5.56	0.004803	3600	222
2.00	0.00	11.11	0.003391	3600	72
3.00	0.00	16.67	0.002833	3600	27
4.00	0.00	22.22	0.003239	3600	59
5.00	0.00	27.78	0.004462	3600	181
6.00	0.01	33.33	0.005248	3600	280
7.00	0.01	38.89	0.005827	3600	363
8.00	0.01	44.44	0.006217	3600	424
9.00	0.02	50.00	0.006798	3600	522
10.00	0.01	55.56	0.006485	3600	468
11.00	0.01	61.11	0.006526	3600	475
12.00	0.01	66.67	0.006532	3600	476
13.00	0.01	72.22	0.006591	3600	486
14.00	0.02	77.78	0.006955	3600	550
15.00	0.01	83.33	0.006672	3600	500
16.00	0.02	88.89	0.006983	3600	555
17.00	0.01	94.44	0.006425	3600	458
18.00	0.01	100.00	0.006718	3600	508
19.00	0.01	105.56	0.006359	3600	447
20.00	0.01	111.11	0.006437	3600	460
21.00	0.00	116.67	0.004689	1800	52
22.00	0.01	122.22	0.006967	1800	138
23.00	0.02	127.78	0.009432	1800	269
24.00	0.02	133.33	0.01069	1800	351
25.00	0.02	138.89	0.010833	1800	361
26.00	0.02	144.44	0.00988	1800	297
27.00	0.01	150.00	0.008539	1800	217
28.00	0.01	155.56	0.008151	1800	196
29.00	0.01	161.11	0.007459	1800	161
30.00	0.01	166.67	0.006532	1800	119

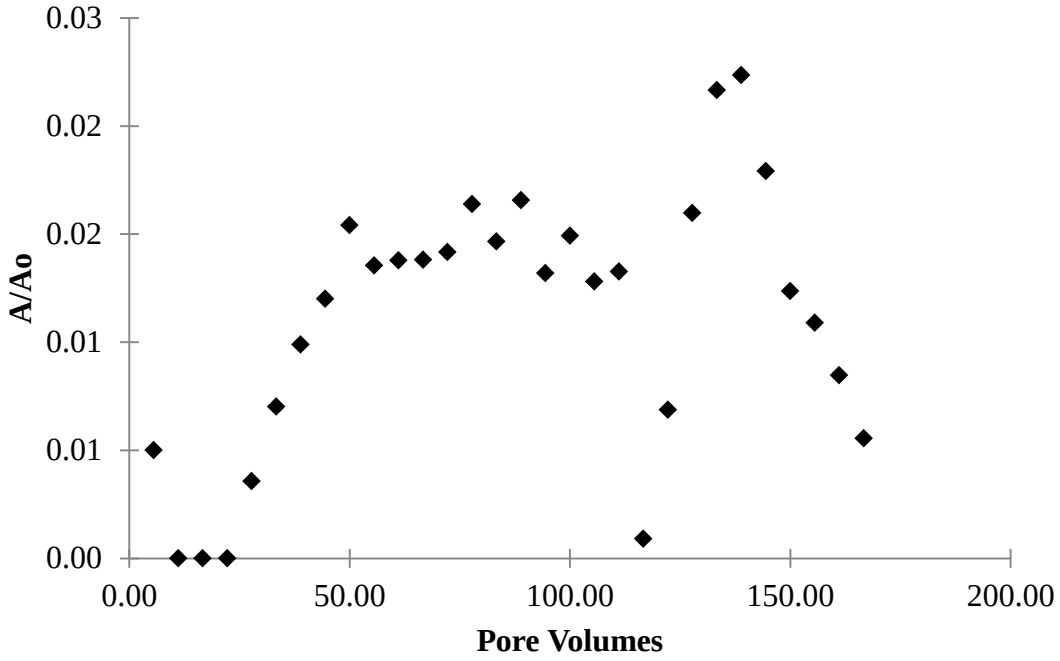


Figure B-1: Graphical representation of the data in Table B-1

Table B-2: Raw data for k' of Pb resin in 2M HCl in 5mm diameter Teflon tubing without extended stoppage of flow (count time= 3600s, background = 12 counts)

	A/A_o	Pore Volume	$\sigma_{A/A0}$	Counts
1.00	0.0015	3.85	0.002899851	32
2.00	0.0017	7.69	0.002952588	36
3.00	0.0050	11.54	0.003767781	107
4.00	0.0081	15.38	0.004400673	174
5.00	0.0111	19.23	0.004945555	240
6.00	0.0143	23.08	0.005450269	308
7.00	0.0162	26.92	0.005739876	350
8.00	0.0128	30.77	0.005226228	277
9.00	0.0166	34.62	0.005800053	359
10.00	0.0146	38.46	0.005499596	315
11.00	0.0177	42.31	0.005951076	382
12.00	0.0175	46.15	0.005918573	377
13.00	0.0165	50.00	0.005780064	356
14.00	0.0164	53.85	0.005773385	355
15.00	0.0149	57.69	0.005541527	321
16.00	0.0129	61.54	0.005233605	278
17.00	0.0132	65.38	0.005284954	285
18.00	0.0154	69.23	0.005617587	332
19.00	0.0121	73.08	0.005106749	261
20.00	0.0140	76.92	0.005407631	302
21.00	0.0150	80.77	0.005569305	325
22.00	0.0144	84.62	0.005471464	311
23.00	0.0138	88.46	0.00537184	297
24.00	0.0121	92.31	0.005114299	262
25.00	0.0115	96.15	0.005007575	248
26.00	0.0103	100.00	0.004811111	223
27.00	0.0113	103.85	0.004984408	245
28.00	0.0107	107.69	0.004874841	231
29.00	0.0093	111.54	0.004631335	201
30.00	0.0086	115.38	0.004504648	186
31.00	0.0131	119.23	0.005270334	283
32.00	0.0105	123.08	0.004843081	227
33.00	0.0111	126.92	0.004945555	240
34.00	0.0088	130.77	0.004530269	189
35.00	0.0077	134.62	0.004338871	167
36.00	0.0091	138.46	0.004589494	196
37.00	0.0106	142.31	0.004858987	229
38.00	0.0089	146.15	0.004564206	193
39.00	0.0095	150.00	0.0046728	206
40.00	0.0129	153.85	0.005240971	279

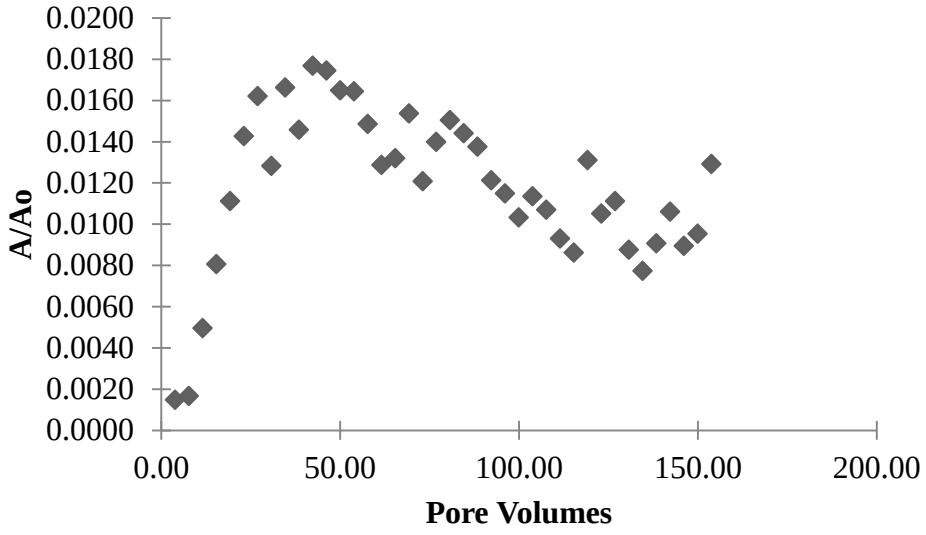


Figure B-2: Graphical representation of the data in Table B-2

Table B-3: Raw data for k' determination for Pb resin in 2M HCl in 5mm diameter Teflon tubing with stoppage of flow (count time = 1900s, background = 12 counts)

Volume	A/A_o	Pore Volume	$\sigma_{A/A0}$	Counts
2.00	0.0000	3.49	0.003088868	13
4.00	0.0000	6.98	0.002997848	11
6.00	0.0042	10.47	0.004661488	57
8.00	0.0153	13.96	0.007395503	176
10.00	0.0255	17.45	0.009228455	286
12.00	0.0250	20.94	0.009137961	280
14.00	0.0266	24.43	0.009406831	298
16.00	0.0287	27.92	0.009725362	320
18.00	0.0275	31.41	0.009538425	307
20.00	0.0239	34.90	0.008969684	269
22.00	0.0236	38.39	0.008907705	265
24.00	0.0197	41.88	0.008245596	224
26.00	0.0226	45.38	0.008750835	255
28.00	0.0471	48.87	0.012224169	518
30.00	0.0582	52.36	0.013505343	637
32.00	0.0426	55.85	0.011655767	469
34.00	0.0292	59.34	0.009796311	325
36.00	0.0245	62.83	0.009061859	275
38.00	0.0178	66.32	0.007884966	203
40.00	0.0188	69.81	0.008075876	214
42.00	0.0122	73.30	0.006749236	143
44.00	0.0141	76.79	0.007147892	163
46.00	0.0134	80.28	0.007010941	156
48.00	0.0132	83.77	0.006971318	154
50.00	0.0112	87.26	0.006519593	132
52.00	0.0135	90.75	0.007030669	157
54.00	0.0102	94.24	0.006281561	121
56.00	0.0084	97.73	0.005847636	102
58.00	0.0090	101.22	0.006011148	109
60.00	0.0117	104.71	0.006645837	138
62.00	0.0086	108.20	0.005894817	104
64.00	0.0115	111.69	0.006583018	135
66.00	0.0133	115.18	0.006991158	155
68.00	0.0126	118.67	0.006830829	147
70.00	0.0117	122.16	0.006645837	138
72.00	0.0113	125.65	0.006540803	133
74.00	0.0095	129.14	0.006125271	114
76.00	0.0091	132.64	0.006034146	110
78.00	0.0065	136.13	0.005353007	82
80.00	0.0061	139.62	0.005222034	77

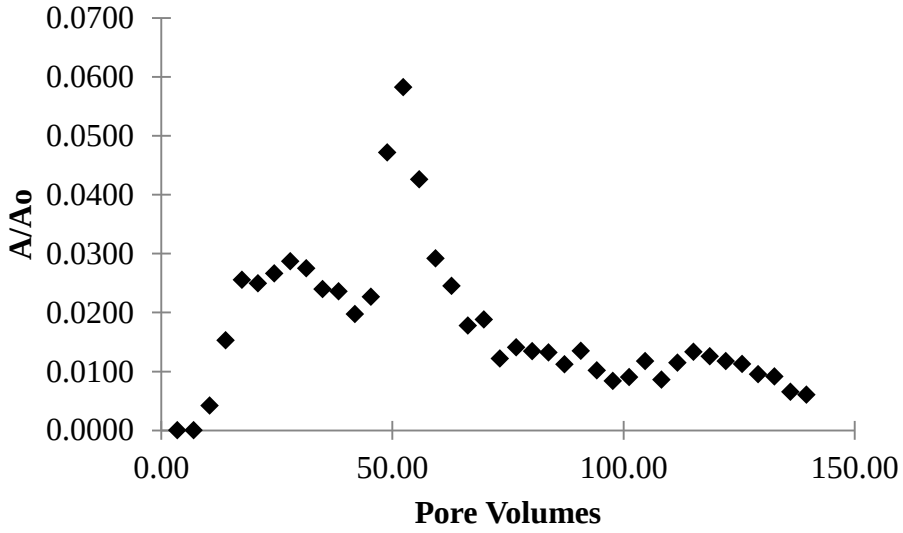


Figure B-3: Graphical representation of the data in Table B-3

Table B-4: Raw data for repeat of k' determination for Pb resin in 2M HCl in 5 mm diameter Teflon tubing with no extended stoppage of flow (count time = 3600s, background = 12 counts)

Volume	A/A_o	Pore Volume	$\sigma_{A/A0}$	Counts
2.00	0.0000	4.38	0.002664	15
4.00	0.0000	8.75	0.002764	22
6.00	0.0000	13.13	0.00262	12
8.00	0.0001	17.51	0.002664	15
10.00	0.0047	21.88	0.003778	108
12.00	0.0143	26.26	0.005415	303
14.00	0.0207	30.63	0.006279	434
16.00	0.0270	35.01	0.007016	561
18.00	0.0278	39.39	0.007109	578
20.00	0.0310	43.76	0.007448	642
22.00	0.0278	48.14	0.007109	578
24.00	0.0317	52.52	0.007526	657
26.00	0.0347	56.89	0.007832	718
28.00	0.0321	61.27	0.007561	664
30.00	0.0295	65.65	0.007291	612
32.00	0.0313	70.02	0.007479	648
34.00	0.0289	74.40	0.007222	599
36.00	0.0268	78.77	0.006994	557
38.00	0.0267	83.15	0.006989	556
40.00	0.0227	87.53	0.006514	473
42.00	0.0242	91.90	0.006695	504
44.00	0.0224	96.28	0.006479	467
46.00	0.0216	100.66	0.006383	451
48.00	0.0215	105.03	0.006371	449
50.00	0.0196	109.41	0.00613	410
52.00	0.0198	113.79	0.006161	415
54.00	0.0207	118.16	0.006279	434
56.00	0.0186	122.54	0.006003	390
58.00	0.0200	126.91	0.00618	418
60.00	0.0228	131.29	0.006526	475
62.00	0.0185	135.67	0.005996	389
64.00	0.0161	140.04	0.005665	339
66.00	0.0147	144.42	0.005464	310
68.00	0.0143	148.80	0.005415	303
70.00	0.0149	153.17	0.005507	316
72.00	0.0131	157.55	0.005241	279
74.00	0.0127	161.93	0.005182	271
76.00	0.0096	166.30	0.004689	208
78.00	0.0089	170.68	0.004564	193
80.00	0.0098	175.05	0.004722	212

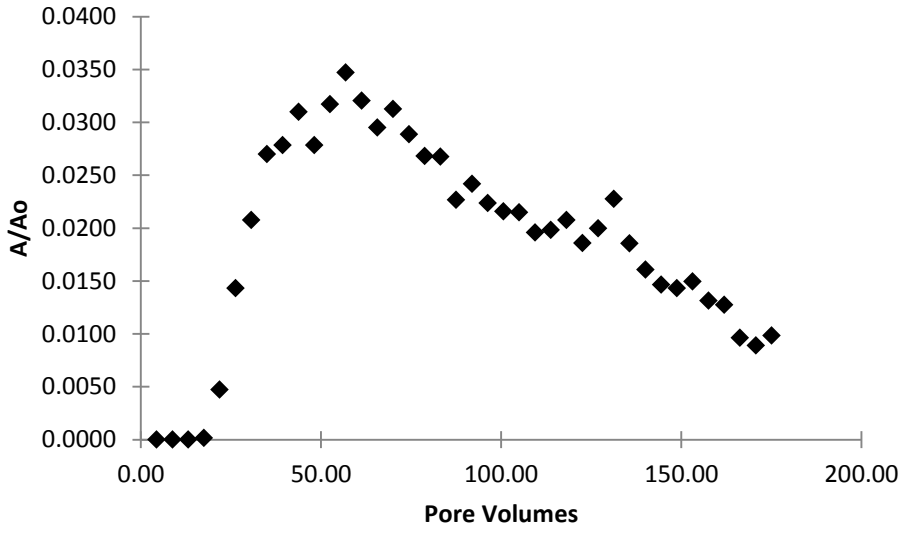


Figure B-4: Graphical representation of the data in Table B-4

B-2 Differences in water obtained from Nevada

Two bottles of groundwater were obtained from the same location in Lahontan Valley, Nevada. Differences were observed in the concentrations in these two bottles for gross alpha concentration determination and ^{210}Po determination on the alpha spectrometer. These differences can be observed below in Table B-5 and B-6. Bottle two was used for the comparison of the novel and traditional methods. The methods outlined in Chapter 4 were used for both sets of experiments.

Table B-5: Gross alpha raw data from LSC for Nevada groundwater (background count rate = 3.33E-03 cps, count time = 172000s)

	Counts
Nevada Bottle 1	659
Nevada Bottle 2	1112

Table B-6: Alpha spectrometer raw data for Nevada groundwater (count time = 70000s, activity added = 1.46 Bq, background count rate = 0.029 cpks)

	Counts
Nevada Bottle 1	9859
Nevada Bottle 2	12291

Appendix C: Additional Preliminary Experiments

C-1 Spontaneous Plating

Preliminary experiments were performed using ZnS:Ag and Ni disks for spontaneous deposition of ^{210}Po. The experiment results are found below in Table C-1. These yield experiments were performed using DDI water and a ^{210}Po spike and followed the same procedure found in Chapter 4 for the traditional water samples. A difference in these preliminary experiments was that were performed using a ^{210}Po standard prepared by leaching ^{210}Po from a Ag source with 12M HCl and diluting the solution with DDI water to 2M HCl instead of the ^{210}Po separated from a ^{226}Ra standard. The Ni disks were counted on an alpha spectrometer, while the ZnS:Ag disks were counted using a photomultiplier tube. Yields for spontaneous deposition onto Ni were lower than for Ag, which is consistent with data in the literature.

Good results were obtained for spontaneous deposition on to ZnS:Ag disks at pH 5 in yield experiments. This method was abandoned as isotopic analysis could not be performed using a photomultiplier tube and the mechanism for the spontaneous deposition was unknown.

Table C-1: ZnS:Ag spontaneous deposition plating procedure yield determination

pH	Temperature (˚C)	Flask	Total Yield (%) Ag	ZnS:Ag	Ni
1	80	Glass	90.3*		
1	80	Glass	89.4*		
1	80	Glass	85.1*		
1	80	Glass	72.5*		
1	80	Glass	47.7		31.8
1	80	Glass	55.3		
1	80	Teflon	55.8		
2	80	Glass	8.5		1.6
2	80	Glass	34.2		
2	80	Teflon	20.5		
2	80	Glass	11.6		
2	55	Glass		11.4	
4	55	Glass	2.4	28.9	
5	55	Glass	3.9	54	
5	80	Glass		57.4	
6	55	Glass		11.5	

C-2 Scintillating Extraction Chromatography Resin

Preliminary experiments were performed using a scintillating extraction chromatography resin for isolation and quantification of ^{210}Po. Yield experiments were performed for the scintillating Pb resin in a 5mm Teflon tube and the method used for the novel method yield experiments outlined in Chapter 4; however, counting was performed on a Hidex Triathler after a 5 minute dark adapt, and the ^{210}Po standard used was the leached standard mentioned above. These results are found below in Table C-2. Good results were obtained for these two experiments, and were followed by k' experiments in 1M HNO_3. This experiment also performed by the method outlined in Chapter 4 using a 7

mL Environmental Express column dry packed to 2 mL with scintillating resin. Counting for these experiments was performed on a Hidex Triathler, and the raw data below in Table C-3. The results were not consistent with data previously found so additional retention experiments for 1M HNO_3 and 2M HCl were performed. Effluents from each elution were also collected for these experiments. Five mL of each of the 10 mL elutions was collected, mixed with Optiphase Hi-Safe and counted on the Hidex Triathler. The results from this study are found below in Table C-4 for 1M HNO_3 and Table C-5 for 2M HCl. An experiment was also performed in 2M HCl following the conditions described above with exception that one was performed by first making a resin slurry to reduce channeling before the resin was added to the column. The results from these experiments are found in Table C-6.The high number of counts in the effluent from these experiments indicated that ^{210}Po was not being retained on the resin.

Table C-2: Scintillating Pb Resin Yield Experiment

	Column Background Counts	Column with Spike Counts	Count Time (s)	Activity Spike (Bq)	Counting Efficiency (%)
Column 1	1084	9007	3600	2.36	93.3
Column 2	717	2692	300	7.45	88.4

Table C-3: Raw data for k' test for scintillating Pb resin in 1M HNO_3 (background counts = 811, activity added = 10 Bq, count time = 300s, ε=27.1%)

Elution Volume (mL)	Column Counts
Spike	1624
10	1591
20	1507
30	1347
40	2058
50	1464
60	1665
70	1716
80	1768
90	1824
100	1974
110	4046
120	3536
130	3402
140	3466
150	3524
160	3156
170	1514
180	1836
190	1760
200	2094

Table C-4: Repeat Scintillating Pb resin retention in 1M HNO_3 experiment with elutions (count time = 300s, Activity added = 10 Bq, ε = 23.8%)

	Elution Volume (mL)	Column Counts	Background Counts
Column	Spike	2046	1332
	10	1967	
	20	757	
Effluents	10	13265	8770
	20	13923	

Table C-5: Scintillating Pb resin retention test in 2M HCl raw data (activity added = 10 Bq, ε= 53.3%)

	Elution Volume (mL)	Column Counts	Background Counts	Count Time (s)
Column	Spike	2171	567	300
	10	2899		
	20	1135		
Effluents	10	10232	7953	1200

Table C-6: Scintillating Pb resin retention test in 2M HCl raw data for slurried resin (activity added = 10 Bq)

	Elution Volume (mL)	Column Counts	Background Counts	Count Time (s)
Column	Spike	2204	478	300
	10			
Effluents	10	11976	7953	1200

An additional k' test was performed in 2M HCl with the eluents, in 1mL increments, counted on the on the Perkin Elmer Wallac Quantulus to reduce and provide a more stable background. The raw data from this experiment is found in Table C-7.

High counts were present in the load elution and the first 2 mL indicating that ^{210}Po was not being retained on the resin. Additional changes were made to procedure in an attempt to determine the cause of the poor retention on the resin. The ^{210}Po standard obtained by separation from a ^{226}Ra standard that was used for experiments in the Results and Discussion chapter was used for k' experiments in an attempt to determine if there issues with the leached spike. An alternative batch method process from Horwitz et al. (1994) was also used for k' determination. This experiment utilized batch samples in which the resin is in contact with the acid of desired concentration mixed with ^{210}Po spike. The resin is then separated from the liquid via centrifugation, and an aliquot (0.5 mL of 2 mL) of the liquid remaining is counted by liquid scintillation counting. A volume of liquid is selected such that half of the ^{210}Po activity should be retained in the liquid and half should be retained in the resin. Based on the expected k' for this resin from the literature, two mL of acid and 0.005g of resin were used for these experiments. Data from experiments in 0.1, 0.5, 1, and 2M HCl are found in Table C-8. This data indicated that activity greater than the activity added was present in the aqueous phase. This experiment was repeated with triplicates for each acid concentration, and the raw data from this experiment is found in Table C-9. For each acid concentration only 25% of the ^{210}Po was remaining on the scintillating Pb resin. This method was abandoned based on this data coupled with the data obtained on the Hidex Triathler.

Table C-7: Raw data from k' experiment in 2M HCl for scintillating Pb resin with samples counted on the Quantulus (count time = 3600s, resin weighty = 0.150 g, activity added = 3.41 Bq).

Elution Volume (mL)	Counts
Blank	42
Load	3591
1	6223
2	755
3	259
4	144
5	91
6	78
7	50
8	32
9	28
10	29
11	41
12	27
13	24
14	28
15	33
16	22
17	19
18	23
19	17
20	12
21	30
22	21

Table C-8: Raw data from k' experiment on scintillating Pb resin in 0.1, 0.5, 1, and 2M HCl (background counts = 13, count time = 7200s).

HCl Concentration (M)	Samples Counts	Activity Added (Bq)	Activity Aqueous (Bq)	Percentage of Activity Added (%)
0.1	5244	5.96	2.91	48.76
0.5	6486	6.1	3.60	58.95
1	14378	6.13	7.98	130.19
2	16559	6.05	9.19	151.94

Table C-9 Raw data from triplicate k' experiment on scintillating Pb resin in 0.1, 0.5, 1, and 2M HCl (background = 13 counts, count time = 7200s)

HCl Concentration (M)	Sample	Samples Counts	Activity Added (Bq)	Activity Aqueous (Bq)	Percentage of Activity Added (%)
0.1	1	15954	11.77	8.86	75.24
	2	15675	11.73	8.70	74.18
	3	15721	11.73	8.73	74.40
0.5	1	15688	11.77	8.71	73.99
	2	15636	11.76	8.68	73.80
	3	15997	11.55	8.88	76.88
1	1	15776	11.92	8.76	73.47
	2	15673	12.12	8.70	71.78
	3	15744	11.73	8.74	74.51
2	1	15930	11.65	8.84	75.90
	2	15933	11.76	8.84	75.21
	3	15782	11.65	8.76	75.20

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